STABLE ISOTOPE CHARACTERIZATION AND PROXY RECORDS OF HYPOXIA-SUSCEPTIBLE WATERS ON THE TEXAS-LOUISIANA SHELF

A Dissertation

by

JOSIAH STRAUSS

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

December 2010

Major Subject: Geology

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ABSTRACT

Stable Isotope Characterization and Proxy Records of Hypoxia-Susceptible Waters on the Texas-Louisiana Shelf. (December 2010)

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Chair of Advisory Committee: Dr. Ethan L. Grossman

Hypoxia, with dissolved oxygen levels < 1.4 ml L^{-1}, is a recurring summer feature of Louisiana shelf bottom waters. Stable isotope characterization ($\delta^{18}O$ and δD) of surface waters over the hypoxic zone shows a shift of dominant river influence from the Mississippi River during April to the Atchafalaya in July. Carbon isotopes of dissolved inorganic carbon ($\delta^{13}C_{DIC}$) in bottom waters reveal the respiration of terrestrial organic carbon (OC) at inshore localities of 10 m depth and the respiration of marine OC at depths equal to and greater than 20 m. $\delta^{18}O$ and $\delta^{13}C$ profiles of Louisiana shelf *Conus* shells collected in 1972 show no evidence for summer hypoxia. Comparison with modern *Conus* records reveal a $\delta^{13}C_{DIC}$ reduction during the last four decades associated with intrusion of ^{13}C-depleted fossil fuel CO_2. Summer $\delta^{13}C$ reductions in Texas shelf *Pteria* shells may imply dissolved oxygen (DO) was reduced by ≈0.7 ml L^{-1}, although this may be attributed to influence of Brazos River discharge on shell $\delta^{18}O$ and $\delta^{13}C$. Foraminifera fauna measured in age-calibrated sediments from the Texas shelf reveal a low oxygen conditions on between 1960 and modern sediments. From 1950 to 1960, fauna indicate oxygenated bottom waters. Contemporaneous increases of foraminifera

δ^{13}Cand δ^{18}O suggest this event is associated with severe drought (the Little Dust Bowl). The synchronicity of these data suggests a link between Brazos River discharge and shelf hypoxia.

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CHAPTER I

INTRODUCTION

Hypoxia, or depletion of dissolved oxygen, is a common feature of bays, estuaries, and continental shelves in close proximity to river deltas. It is defined by dissolved oxygen (DO) falling below 2 mg L^{-1} (compared to normal concentrations of 5 - 9 mg l^{-1}) (Pavela et al., 1983). Hypoxia occurs when a stratified water column limits the circulation of bottom waters and prevents them from being oxygenated at the surface. Respiration of organic matter then depletes the bottom waters of DO. Hypoxic conditions are exacerbated by nutrient loading (Rabalais et al., 2002). Nutrients are incorporated into river waters that then flow onto the continental shelf, contributing to phytoplankton blooms. As these blooms flourish, they create a flux of organic matter to the seafloor in the form of copepod fecal pellets and dead plankton, which are oxidized by bacteria, further depleting bottom waters of oxygen (Rabalais et al., 2002b). Within the last half-century, hypoxia has become a major environmental concern. The global number of hypoxic (i.e. dead) zones has doubled every decade since 1960, with prevalence near large population centers (Diaz and Rosenberg, 2008). Historically, hypoxic zones have been mostly limited to semi-enclosed to enclosed bays or silled basins, however more recently they have developed in coastal environments of the Baltic, East China Sea and Gulf of Mexico (Diaz and Rosenberg, 2008).

This dissertation follows the style of Geology.

Hypoxia in the northern Gulf of Mexico extends westward of the Mississippi Delta along the Texas-Louisiana shelf (Rabalais et al., 2001), occasionally extending onto the Texas shelf (Harper et al., 1981). It is the largest hypoxic zone in the western Atlantic, measuring up to 20,000 km^2 and commonly ranging in depth from 5 to 30 m (Rabalais et al., 2001). Louisiana shelf hypoxia is caused by the combined annual discharge of nearly 600 km^3 of nutrient-rich fresh water from the Mississippi and Atchafalaya Rivers (Bianchi and Allison, 2009; Rabalais et al., 2002b). It is a seasonal event prevalent from the late spring to early fall. This seasonality is caused by increased spring discharge combined with a weakening or reversal of the coastal current from shifting winds, which forces pooling of low-salinity shelf waters and allows stratification to develop (DiMarco et al., 2005).

Although the basic requirements for hypoxia formation (i.e. stratification and respiration) are known (Rabalais et al., 2002; Hetland and DiMarco, 2008; Bianchi et al., 2009), the prediction of its size has been problematic. For example, a large disparity between a predicted area of nearly 20,000 km^2 (Scavia et al. 2003) and the measured area of the 2009 hypoxic zone (≈8000 km^2) has recently highlighted the complexity of shelf hypoxia. A better understanding of the relative contributions of freshwater discharge (i.e. Atchafalaya vs. Mississippi) and organic carbon (OC) (i.e. terrestrial vs. marine) to the shelf, can improve the predictability of its formation.

Oxygen and hydrogen stable isotopes ($^{18}O/^{16}O$, D/H) can be used as conservative tracers of water masses (Kendall and McDonnell, 1998 and references therein). The Atchafalaya River encompasses waters from the Mississippi River, Red River and

Louisiana wetlands. The geography of the Red River drainage basin (as compared to the Mississippi River drainage basin) results in less distillation fractionation of precipitation forming cloud vapor (i.e. the raining out of $H_2{}^{18}O$ and ^2H_2O) making its waters ^{18}O and ^2H enriched relative to Mississippi River waters. Additionally, the enhanced evaporation of $H_2{}^{18}O$ and ^2H_2O over the Atchafalaya wetland further increases the $\delta^{18}O$ and δD of Atchafalaya River water. As a consequence the $\delta^{18}O$ and δD of Atchafalaya discharge are $\sim$+1‰ and $\sim$+5‰ respectively enriched relative to Mississippi River waters (Lee and Veizer, 2003). Assuming all river discharge has 0 salinity, these isotopic differences can be used to trace their mixing with seawater (S=36, $\delta^{18}O$ = 1.1‰, δD = 6‰) over the shelf. Thus, the $\delta^{18}O$ and δ^2H characterization of shelf surface waters can identify the dominant source of river discharge that creates or sustains the stratification necessary for hypoxia formation. Chapter II outlines the $\delta^{18}O$ and δD of Louisiana shelf surface waters from April and July of 2008 (i.e. prior to and during hypoxia) to determine the relative influence of the Mississippi and Atchafalaya Rivers on its formation.

In addition to $\delta^{18}O$ and δD, the $\delta^{13}C$ of dissolved organic carbon (DIC) can also be used as tracers of source waters (Kendall and McDonnell, 1998 and references therein), but are less conservative than $\delta^{18}O$ or δD and are thus better suited for measuring chemical (Quay et al., 1992) and biochemical reactions (Farquhar et al., 1989). In Chapter II, the $\delta^{13}C_{DIC}$ has been used as an indicator of the mineralization of organic matter in bottom waters (McCorkle et al., 1985). The influence of bottom water respiration on $\delta^{13}C_{DIC}$ depends on the $\delta^{13}C$ of the organic carbon respired (e.g. terrestrial vs. marine), the source of which is a factor that has recently been contended (Bianchi et

al., 2009; 2010). The contributions of both terrestrial and marine OC sources to shelf waters were exacerbated by human activity in the 20th century. Increased terrestrial OC influence may be associated with modification of the Mississippi Delta by the Army Corps of Engineers (Bianchi et al., 2009), whereas increased marine OC is related to the increase of nutrients in Mississippi and Atchafalaya Rivers (Rabalais et al., 2002). The lack of coastal water chemistry data (i.e. salinity, DO, nutrients) contemporary with these anthropogenic events has limited understanding of the relative consequences of delta modification and extra nutrient delivery.

The initial documentation of Louisiana hypoxia dates back to 1972 (Ward and Stanford, 1979), with the first comprehensive spatial surveys performed in 1975 and 1976 (Turner and Allen, 1982). Occurrences of hypoxia prior to these surveys have been inferred from the distribution of benthic foraminifera in sediment cores (Sen Gupta et al., 1996; Osterman et al., 2008). These records indicate a dramatic increase in hypoxia since about the 1950s, concomitant with increased use of nitrogen-rich fertilizers, particularly anhydrous ammonia. These records, however, fail to capture hypoxia on a yearly resolution.

Gastropod and bivalve mollusks provide multi-year environmental records through $\delta^{18}O$ and $\delta^{13}C$ analyses of incremental shell $CaCO_3$ (Wefer and Berger, 1991; Goodwin et al., 2003). Additionally, observations from the northern Gulf of Mexico hypoxic zones show that bivalves and gastropods can be resilient to low oxygen levels (Rabalais et al., 2001), and thus their shells may contain annually-resolved records of hypoxic conditions. The $\delta^{18}O$ values of mollusk shells are dependent on two variables:

temperature and the $\delta^{18}O$ of ambient seawater (Grossman and Ku, 1986). The $\delta^{13}C$ of shell carbonate is known to track changes in the $\delta^{13}C_{DIC}$ (McConnaughey and Gillikin, 2008). Therefore the lowering of bottom water $\delta^{13}C_{DIC}$ through hypoxia-associated respiration can be recorded within the mollusk shells. Chapter III outlines the environmental interpretations of isotopic records from mollusks retrieved from localities subject to recurrent hypoxia on the Louisiana and Texas shelves. Additionally, mollusks sampled from localities of high freshwater influence and open ocean conditions are compared.

As previously mentioned, long term records (>100 years) of Louisiana shelf hypoxia based on benthic foraminifera from sediment cores have indicated a large increase in the size and severity of seasonal hypoxia since roughly the 1950s (Sen Gupta et al., 1996; Osterman et al., 2008). Such records for the middle Texas shelf have yet to be produced. An increase in the occurrence of Texas shelf hypoxia may be associated with mid-20th century exacerbation of Louisiana shelf hypoxia; however hypoxia measured on the middle Texas shelf during the summer of 2007 was chemically linked to increased discharge of the Brazos River (DiMarco et al., submitted).

The discovery of Brazos River associated hypoxia has highlighted the contribution of smaller, more localized rivers to Gulf of Mexico hypoxia. Chapter IV documents a 100-year record of low oxygen bottom waters influenced by Brazos River discharge based on the abundance and stable isotopic records of benthic foraminifera. Benthic conditions are interpreted using the relative abundances of the low oxygen tolerant *Ammonia* to the more normoxic *Elphidium* (Sen Gupta et al., 1996). Similar to

mollusk shells, $\delta^{18}O$ and $\delta^{13}C$ of individual and small groups of foraminifera are indicative of temperature, fresh water influence and benthic respiration. Thus, stable isotopes of foraminifera can provide additional insight into bottom water conditions.

CHAPTER II

STABLE ISOTOPE CHARACTERIZATION OF HYPOXIA-SUSCEPTIBLE WATERS ON THE LOUISIANA SHELF: TRACING FRESHWATER DISCHARGE AND BENTHIC RESPIRATION

Overview

Hypoxia, with dissolved oxygen levels < 1.4 mL L^{-1}, is a recurring summer feature of Louisiana shelf bottom waters. To examine the sources of freshwater and carbon cycling associated with Louisiana shelf hypoxia, we measured $\delta^{18}O$, δD, $\delta^{13}C$ of dissolved inorganic carbon (DIC), salinity and dissolved oxygen (DO) in waters from 37 stations during April and July of 2008. Seafloor $\delta^{18}O$ values resemble typical Gulf of Mexico seawater (≈ 1.1‰) while surface waters values are substantially lower (e.g., < -2.0‰) due to mixing with river-sourced freshwater. Salinity-$\delta^{18}O$ regressions of 2008 surface waters show the $\delta^{18}O$ of discharge to average -6.8‰ in April and -5.1‰ in July. Mass balance calculations using $\delta^{18}O$ show the relative contributions of Mississippi and Atchafalaya Rivers to shelf waters were 53±30% and 47±30% during April. An increase in $\delta^{18}O$ and δD of freshwater discharge from April to July of 2008 is suggestive of a stronger influence by the Atchafalaya basin waters on the shelf during summers, a trend that coincides with a known coastal current reversal. The $\delta^{13}C_{DIC}$ of surface water varies from -5.0 to 1.2‰ and correlates with salinity indicating mixing of seawater and river water. The $\delta^{13}C_{DIC}$ of sub-pycnocline water ranges from -2.3 to 0.3‰, with lower values reflecting enhanced respiration. Mass balance calculations based on $\delta^{13}C_{DIC}$ and DO

relationships suggest that shallow bottom waters (depth ≈ 10 m) are made hypoxic by respiration of terrestrially sourced organic carbon (OC), while bottom waters in depths of 20 m and greater are made hypoxic through respiration of marine OC. The $\delta^{13}C_{DIC}$-DO trends of middle-depth waters (≈10 m) along the 20 m isobath indicate water column respiration of an as yet unresolved OC source.

Introduction

Hypoxia, or depletion of dissolved oxygen, is a common feature of bays, estuaries, and river-dominated continental margins (Rabalais and Turner, 2001). Hypoxia is defined by dissolved oxygen (DO) concentrations below 1.4 mL L^{-1} (compared with normal concentrations between 4 and 6 mL L^{-1})(Pavela et al., 1983; Rabalais et al., 2001b). Hypoxia occurs when the water column becomes stratified from the convergence of water masses of different salinities, and then sub-pycnocline respiration of organic matter depletes DO.

In the last century, hypoxia has become a major environmental concern. The global number of hypoxic zones has doubled every decade since 1960, with prevalence near large population centers (Diaz and Rosenberg, 2008). Historically, hypoxic zones have been mostly limited to semi-enclosed to enclosed bays or basins, however more recently they have developed in coastal seas such as the Baltic Sea, East China Sea and Gulf of Mexico. The occurrence of hypoxia is promoted by nutrient-loading (Turner and Rabalais, 1994; Rabalais et al., 2002b; Conley et al., 2009). Nutrients from man-made fertilizers run-off into river water and are fluxed onto the continental shelf, creating or

contributing to phytoplankton blooms (Mitsch et al., 2008; Rabalais et al., 1999). As these blooms flourish, they flux organic matter to the seafloor in the form of copepod fecal pellets and dead plankton, which are respired by bacteria, depleting bottom waters of oxygen.

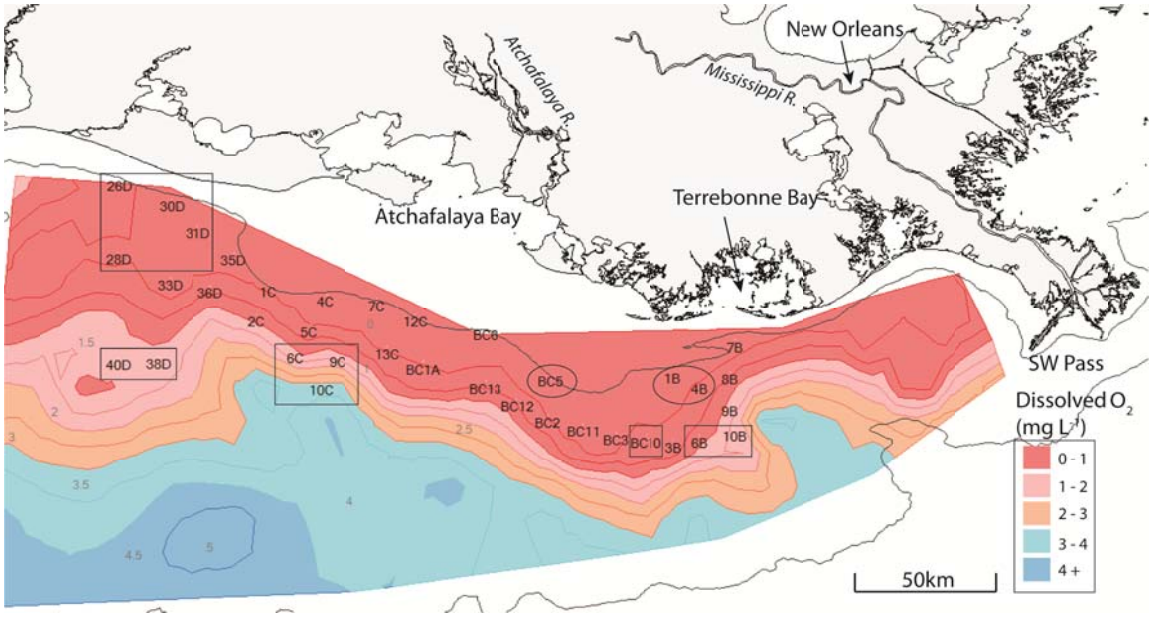

Figure 1: Map of April and July 2008 sampling stations and bottom water DO concentration on the Louisiana shelf. Stations enclosed in boxes were only sampled in July; stations encircled were only sampled in April. Contours of dissolved O_2 (interval = 0.5 mg L^{-1}) represent observations during July NOAA SEAMAP cruises aboard R/V Oregon II. Bathymetric contours of 10 m and 200 m are illustrated.

In the Gulf of Mexico (GoM), hypoxia is prevalent along the Louisiana and northern Texas shelf, at depths not usually exceeding 30 m (Rabalais et al., 2001; Bianchi et al.,

2010). Hypoxia extends westward of the Mississippi Delta along Louisiana coastal waters, occasionally encroaching upon the middle Texas shelf (Harper et al., 1981). This is the largest coastal hypoxic zone on the western Atlantic, measuring up to 20,000 km^2 (Rabalais et al., 2001). The hypoxia is caused by the annual influx of nearly 600 km^3 of nutrient-rich freshwaters from the Mississippi River and Atchafalaya Rivers. It occurs seasonally from late spring to early fall during a confluence of peak river discharge from spring rains, weakening of wind-driven coastal currents, limited wave activity, and increased solar intensity, creating conditions favorable for phytoplankton blooms and water column stability (Wiseman et al., 1997; Rabalais et al., 2001; Bianchi et al., 2010)

Better understanding of the relative influences of the sources of freshwater (i.e. Atchafalaya vs. Mississippi) and organic carbon (OC) (i.e. terrestrial vs. marine) on the formation of Louisiana shelf hypoxia can improve the predictability of its formation (Justić et al., 2007). For example, a large disparity between a predicted area of nearly 20,000 km^2 (gulfhypoxia.net) and the measured area of the 2009 hypoxic zone (≈8000 km^2, see Figure 1) has highlighted the complexity of shelf hypoxia. Discharge from the Mississippi and Atchafalaya Rivers, the primary sources of freshwater on the Louisiana continental shelf (Dinnel and Wiseman, 1986), is the principal driver of water column stratification and nutrient input. The Atchafalaya River diverges from the Mississippi River at the Old River Control Structure, where 70% of the combined flow of the Mississippi and Red Rivers is distributed to the Mississippi and 30% is distributed to the Atchafalaya. Because the discharge of both rivers is derived from the same terrestrial sources, the rivers are frequently considered a single freshwater influence (Rabalais et

al., 2002b) and as point sources of nutrient export (Scavia et al., 2003; Turner et al., 2006; Scavia and Donnelly, 2007). More recently, a hydrodynamic circulation numerical model has shown spatially separated hypoxia regions east and west of Terrebonne Bay, with stratification in the eastern zone associated with the Mississippi River discharge, and stratification in the western zone influenced by runoff from the Louisiana Bight and Atchafalaya River (Hetland and DiMarco, 2008).

Here we use oxygen and hydrogen stable isotopes ($^{18}O/^{16}O$, D/H) of Louisiana shelf waters during a period of hypoxia and peak spring discharge to examine the relative influence of the Mississippi and Atchafalaya Rivers on fresh water spatial distribution and hypoxia formation. While salinity has traditionally been used to trace freshwater masses, O and H isotopes improve on the measure by providing a tracer for freshwaters from different drainage basins, and have been extensively utilized to trace freshwater sources in coastal seas (Frank, 1972; Redfield and Friedman, 1969; Torgersen, 1979; Wagner and Slowey, 2011). The method relies on the fact that the oxygen and hydrogen isotope compositions of river waters are dependent upon drainage basin geography and evaporative flux of river water. Due to Rayleigh distillation, drainage basins of lower latitudes exhibit higher $\delta^{18}O$ values than the more isotopically "rained out" high latitude drainage basins (Kendall and Coplen, 2001). Oxygen and hydrogen isotopes of Atchafalaya River water are consistently high relative to Mississippi River water due to the incorporation of Red River drainage (average $\delta^{18}O$ = -3.6‰ and δD = -19.2‰), and possibly due to enhanced evaporation over the Atchafalaya floodplain (Coplen and Kendall, 2000; Lee and Veizer, 2003).

Freshwater discharge onto continental shelves also causes variations in the carbon isotope composition of dissolved inorganic carbon ($\delta^{13}C_{DIC}$; Kendall and McDonnell, 1998; Mackensen, 2001; Pierre et al., 1991). However, the $\delta^{13}C_{DIC}$ will also vary in response to photosynthesis, respiration, upwelling, and exchange with atmospheric CO_2 (Quay et al., 2003), and can serve as a tracer for carbon cycling. On the Louisiana shelf bottom, the dominant process controlling carbon cycling in bottom waters is respiration (Dortch et al., 1994). As is typical of river-dominated ocean margins (RioMARS), turbidity on the eastern Louisiana shelf generally limits photosynthesis to the upper 10 m of the water column (Lohrenz et al., 1990; Dagg et al., 2004; Dagg et al., 2005; Bianchi and Allison 2009). Additionally, stratification of the water column limits the influence of atmospheric CO_2 on the $\delta^{13}C_{DIC}$ of bottom waters. The influence of bottom water respiration on $\delta^{13}C_{DIC}$ depends on the $\delta^{13}C$ of the organic carbon respired (e.g. terrestrial vs. marine). Thus, carbon isotopes can help trace organic carbon sources, an important and contended factor in the development of hypoxic waters (Dagg et al., 2004; Geen et al., 2006; Bianchi et al., 2009, 2010).

Methods

Waters were collected on two cruises to the Louisiana shelf during April and July of 2008 on the R/V Pelican, a ship operated by the Louisiana Universities Marine Consortium (LUMCON). Sampling stations were west of the Mississippi delta in commonly hypoxic shelf waters off Terrebonne and Atchafalaya Bays (Fig. 1). Water samples were collected using a Rosette equipped with six 4 L Niskin bottles and a hand-

deployed bucket for surface samples. Niskin bottles were tripped at 5 m intervals beginning at the seafloor and ending at the surface.

Analyses of $\delta^{18}O$ and $\delta^{13}C_{DIC}$ were performed on samples collected at 5 m and 10 m depth increments, respectively. The vertical sampling increments crossed horizontal density gradients. δD analyses were performed on surface waters. Water samples collected for analysis of $\delta^{18}O$ and δD were either stored in 15 mL vials with septa caps or 10 mL Vacutainer™ brand pre-evacuated blood sampling vials. Screw top vials were wrapped with electrical tape to minimize evaporation effects. Samples were stored on ice in the field and refrigerated following transport to the university. $\delta^{13}C_{DIC}$ samples require specific handling to preclude degassing or microbial production of CO_2. $\delta^{13}C_{DIC}$ samples were stored in pre-evacuated (30 to 60 millitorr) 25 mL serum bottles pre-poisoned with $HgCl_2$ capped with 20 mm thick septum stoppers (Bellco™ 2048-11800) sealed with aluminum crimps. Once collected, $\delta^{13}C_{DIC}$ samples were stored on ice in the field and kept refrigerated in the laboratory.

Derived salinity and DO were measured in the field using a Seabird SBE 911plus CTD profiling instrument and a Seabird SBE 43 dissolved oxygen sensor, respectively. Accuracy of salinity measurements were confirmed through water sample analyses using a Guildline Autosal salinometer provided by the Geochemical and Environmental Research Group (GERG) at TAMU; DO measurements were verified by Winkler titration at selected stations and depths.

Water samples were analyzed for $\delta^{18}O$, δD, and $\delta^{13}C_{DIC}$ at the Texas A&M University's Stable Isotope Geosciences Facility. The $\delta^{18}O$ analyses were carried out

using an equilibration method, where 250 µL aliquots of water were injected into an airtight vial filled with 99.7% He and 0.3% CO_2. Waters were equilibrated for two days at a constant temperature of 22°C. Water samples were analyzed for $\delta^{13}C_{DIC}$ by acidifying 500 µL aliquots of seawater with 50 µL of phosphoric acid in an airtight exetainer vial flushed with ultra-high purity He (Torres et al., 2005). Headspace CO_2 of both $\delta^{18}O$ and $\delta^{13}C_{DIC}$ prepared vials were analyzed using a Thermo Finnigan DeltaPlusXP Isotope Ratio Mass Spectrometer attached to a GasBench II automated gas preparation and delivery system. $\delta^{18}O$ measurements were standardized using Vienna Standard Mean Ocean Water (VSMOW) reference water ($\delta^{18}O$ = 0‰); precision of standards was at or better than 0.06‰. $\delta^{13}C_{DIC}$ measurements were standardized using NBS-19 reference material ($\delta^{13}C$ = 1.95‰) and average precision of standards was at or better than 0.07‰. Precision of $\delta^{13}C_{DIC}$ measurements was verified using an internal $NaHCO_3$ solution. The precision of this reference solution was at or better than 0.08‰. Measurements of water δD were made by automated injection into a Thermo Finnigan TC/EA according to the methods of Morrison et al. (2001). The H_2 gas evolved from pyrolosis at 1400°C was measured on a Thermo Finnigan DeltaPlusXP with a precision of ±1‰ standardized to VSMOW reference water (δD = 0‰).

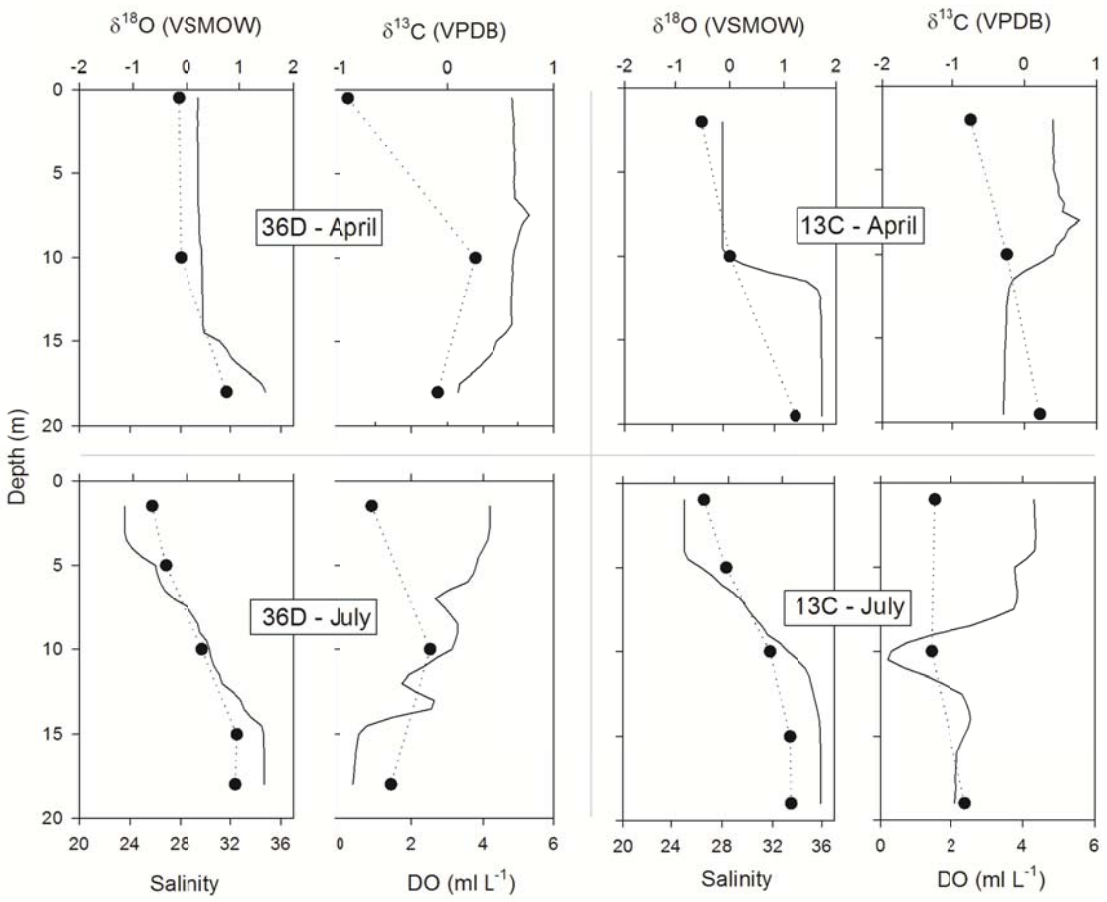

Figure 2: Depth profiles of selected April and July stations. Solid lines denote salinity and DO; dotted lines represent isotopic data, with black circles signifying each measurement. Note the strong stratification observed in April shelf waters, which is especially apparent at station 13C. On the contrary, July stratification weak and salinity and $\delta^{18}O$ gradients are gradual.

Results

Salinity profiles for April waters reveal a well-defined pycnocline between 10 and 13 m depth in water depths of 15 m or greater (Fig. 2). Shallower waters were vertically mixed. Salinities ranged from 22 to 32 above the pycnocline and from 34 to 36 in sub-pycnocline waters. During July, the pycnocline was not as well defined and salinities increased steadily with depth. Salinities increased with depth gradually with values ranging from 12 to 36 along the 20 m isobath. Bottom waters on the 10 m isobath showed slightly mixed salinities ranging from 30 to 36.

April and July DO values indicate bottom waters became hypoxic between late April and July. In April, hypoxia was measured at stations 1B and 4B on the inner shelf offshore of Terrebonne Bay. July DO showed widespread hypoxia between 10 and 30 m isobaths west of Terrebonne Bay. In addition to these data, data collected from June-July, 2008 by the NOAA Southeastern Monitoring and Assessment Program (SEAMAP) cruises aboard the *R/V Oregon II* also showed hypoxia in 10-30 m depths from west of the Mississippi River delta onto the middle Texas coast (Fig. 1).

Oxygen isotopes show similar spatial patterns as those observed in salinity data (Fig. 2). Louisiana shelf surface waters were generally depleted in ^{18}O due to discharge of freshwater and formation of stratification in the late spring and summer. April surface waters exhibited an average $\delta^{18}O$ of -0.7‰ and ranged between -1.8 and 0.7‰, while July surface waters averaged -1.0‰ and ranged from -3.5 to 0.2‰. Low salinity (20-30) and $\delta^{18}O$ (-2 to 0‰) waters penetrated up to 10 m depth (i.e. near the depth of the pycnocline) during both April and July (Fig. 2). Below the pycnocline, values were

typically characteristic of offshore Gulf of Mexico waters, where salinity ranges from 34 to 36 and $\delta^{18}O \approx 1.1‰$ (J. Strauss, unpublished data; Wagner and Slowey, 2011). Hydrogen isotopes of surface waters exhibit larger ranges than oxygen isotopes due to greater fractionation factors during evaporation and precipitation (Craig, 1961). During April, δD values ranged from -11 to 3‰ and averaged -5±1‰. Similar to $\delta^{18}O$ trends, July δD values were lower than April values, exhibiting a range from -23 to 0‰ and an average of -8±1‰.

Spatial distributions of surface salinity and $\delta^{18}O$ are illustrated in Figure 3. April and July exhibit contrasting distributions. April contours show a meandering inshore front of low salinity and $\delta^{18}O$ surface waters. This front lies west of Terrebonne Bay and extends seaward from Atchafalaya Bay. Both salinity and $\delta^{18}O$ increase with distance from shore. July contours show a different pattern with variability mostly alongshore and waters of progressively decreasing salinity and $\delta^{18}O$ eastward from the westernmost Louisiana shelf to offshore Terrebonne Bay. The salinity and $\delta^{18}O$ patterns during 2008 match trends observed during April and August of 1994 (Jochens et al., 1998; Zerai, 2001). Scatter plots show strong correlations between $\delta^{18}O$ and salinity and δD and salinity of surface waters (Fig. 4; Table 1:Eqns. 1-4). The $\delta^{18}O$ and δD relationships with salinity for April yield higher slopes relative to July months and give y-intercepts (where salinity = 0) of -6.5‰ and -38‰ respectively. July salinity-$\delta^{18}O$ and salinity-δD relationships exhibit lower slopes and higher y-intercepts of -4.7‰ and -29‰ respectively. These values identify the $\delta^{18}O$ and δD of the fresh water being mixed with shelf surface waters.

The $\delta^{13}C_{DIC}$ of Louisiana shelf waters can be partitioned into two groups, surface waters above the pycnocline that are heavily influenced by river discharge and exchange with atmospheric CO_2, and waters below the pycnocline that are influenced by respiration. April surface waters a ranged from -1.0 to 1.2‰ and averaged 0‰. April surface water $\delta^{13}C_{DIC}$ values did not correlate with salinity, and were thus more affected by exchange with atmospheric CO_2. July surface water $\delta^{13}C_{DIC}$ positively correlate with salinity ($r^2 = 0.79$). The July surface waters influenced by fresh water runoff exhibited the lowest $\delta^{13}C$ values that ranged from -5.0 to 0‰ and averaged of -1.6‰. (Figure 5; Table 1: Eqns. 5-6).

Table 1: Selected regressions of stable isotope measurements, DO and salinity.

Eqn	Sample Set	y	b (*SE*)	x	y-intercept(*SE*)	r^2	Sample location	Outliers Removed
1	April Surface	$\delta^{18}O$	0.21 (±0.01)	Salinity	-6.5 (±0.4)	0.92	Surface	
2	July surface	$\delta^{18}O$	0.17 (±0.01)	Salinity	-4.70 (±0.17)	0.95	Surface	
3	April Surface	δD	1.22 (±0.08)	Salinity	-38 (±2.4)	0.99	Surface	
4	July surface	δD	1.0 (±0.07)	Salinity	-29 (±1.6)	0.92	Surface	9C
5	April surface	$\delta^{13}C_{DIC}$	0.09 (±0.06)	Salinity	-2.5 (±1.7)	0.13	Surface	
6	July surface	$\delta^{13}C_{DIC}$	0.5 (±0.02)	Salinity	-4.95 (±0.45)	0.72	Surface	9B, 7B, 3B, BC10
7	April 20 m isobath	$\delta^{13}C_{DIC}$	1.02 (±0.27)	DO	-3.07 (±0.05)	0.53	Bottom	
8	July 10 m isobath	$\delta^{13}C_{DIC}$	0.66 (±0.17)	DO	-2.20(±0.18)	0.7	Bottom	
9	July 20 m isobath	$\delta^{13}C_{DIC}$	0.26 (±0.07)	DO	-1.1 (±0.1)	0.41	Bottom	
10	April and July 20 m isobath	$\delta^{13}C_{DIC}$	0.37 (±0.03)	DO	-1.13(±0.08)	0.82	Bottom	
11	July transitional waters	$\delta^{13}C_{DIC}$	0.27 (±0.04)	DO	-1.43(±0.13)	0.65	Transition	

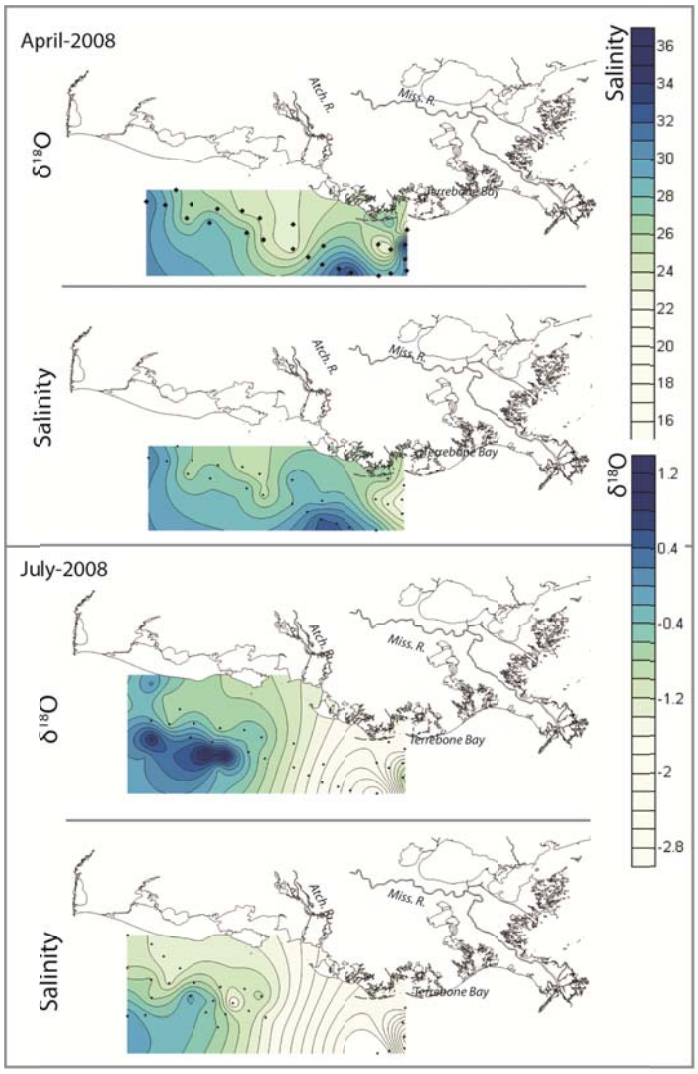

Figure 3: Color contour plots of surface water $\delta^{18}O$ and salinity. Contours are interpolated using kriging method (using default parameters) in Golden Software Surfer 9 (Golden Software Inc., Golden, USA). April waters are characterized by movement of low salinity, low $\delta^{18}O$ waters westward along the shelf. In July the reversal of the coastal current pushes low salinity, low $\delta^{18}O$ waters further offshore, changing the orientation of contour lines. Under summer circulation, the potential for Atchafalaya River influence on the shelf is dramatically increased.

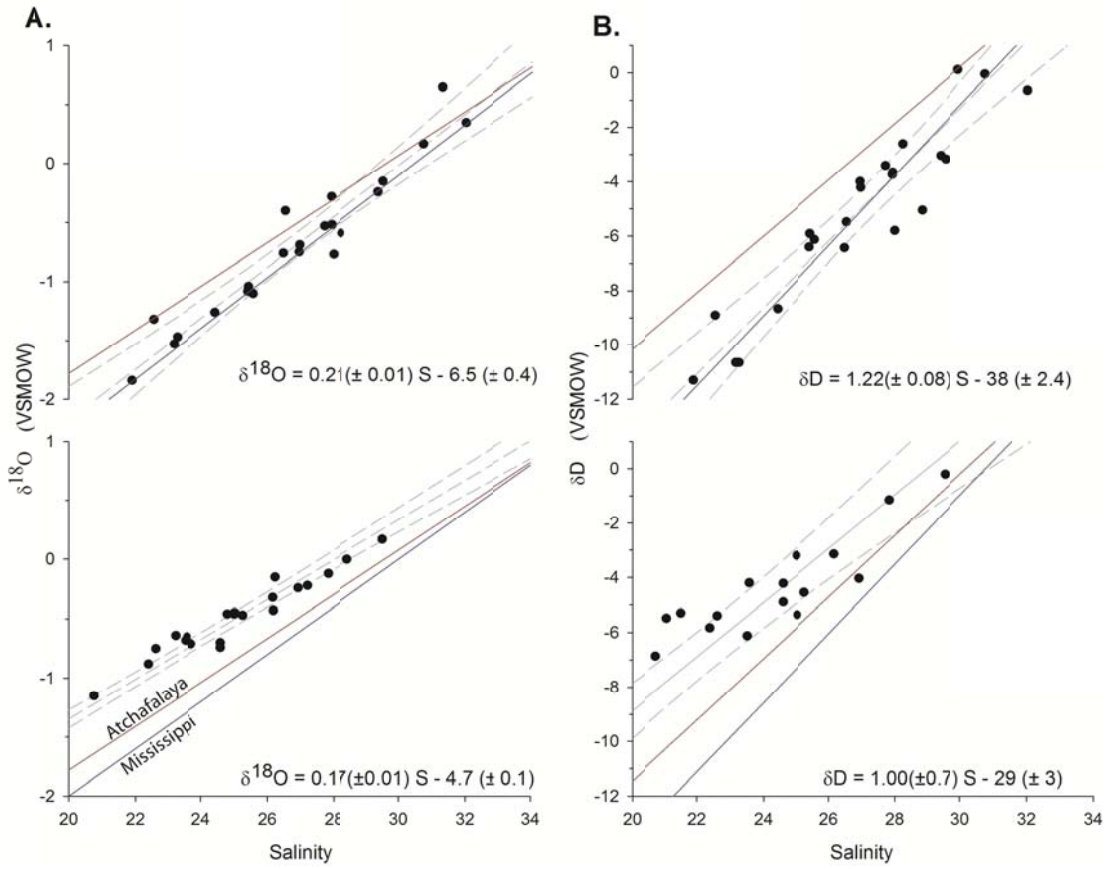

Figure 4: A. $\delta^{18}O$-Salinity plots for April (top) and July (bottom) surface waters. **B.** δD-Salinity plots for April (top) and July (bottom) surface waters. All plots show mixing lines for Atchafalaya (red) and Mississippi River (blue) waters for the month in which marine waters were sampled based on the average $\delta^{18}O$ and δD values at inland stations of the US Geological Survey's National Stream Quality Accounting Network (NASQAN) . Regression and 99% confidence intervals are shown in grey lines. The higher values for July δD and $\delta^{18}O$ are likely the result of enhanced evaporation of Atchafalaya freshwaters downstream of USGS river sampling stations.

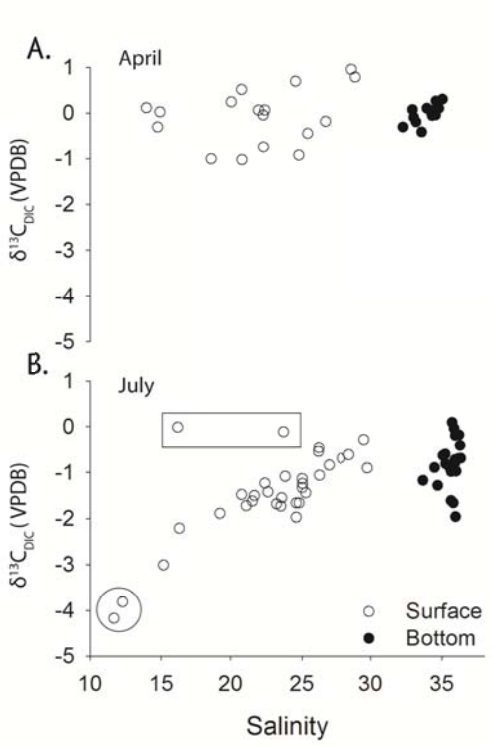

Figure 5: $\delta^{13}C_{DIC}$ and salinity plots of surface and bottom waters from **A.** April and **B.** July Louisiana shelf cruises. April surface waters appear to show the effects of atmospheric exchange. July surface water $\delta^{13}C_{DIC}$ values correlate with salinity, highlighting the influence of freshwater mixing on $\delta^{13}C_{DIC}$ of shelf waters. Values enclosed in the rectangle represent outliers that are likely influenced by exchange with atmospheric CO_2. Encircled values are from easternmost stations outside Terrebonne Bay and may represent Mississippi River water influence. A freshwater $\delta^{13}C_{DIC}$ of -5.0‰ can be estimated from the y-intercept of the July salinity-$\delta^{13}C_{DIC}$ regression (excluding enclosed values). Bottom waters salinities do not vary, whereas $\delta^{13}C_{DIC}$ variability in bottom waters results from respiration (Fig. 6).

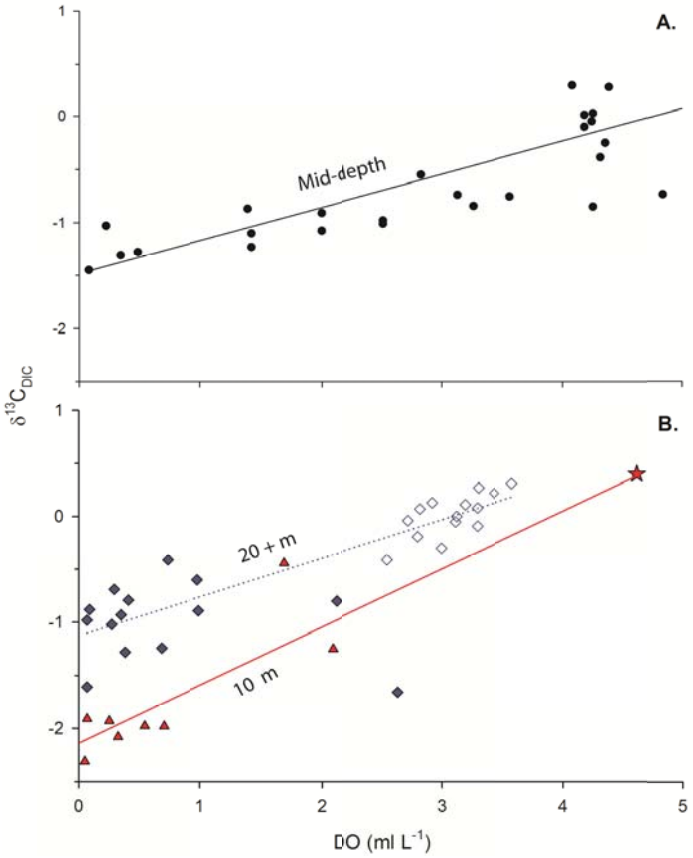

Figure 6: A. DO and $\delta^{13}C_{DIC}$ for transitional depth (10±1 m) waters in depths of 20-30 m. The trend here is indicative of water column respiration. Mixing of oxygenated waters above the pycnocline obscure $\delta^{13}C_{DIC}$ values so that a calculation of $\delta^{13}C_{Res}$ is not possible. **B.** DO and $\delta^{13}C_{DIC}$ of shelf bottom waters on the 20-30 m (diamonds) and 10 m (triangles) isobaths. For these samples, a correlation is drawn through April (open diamonds) and July (closed diamonds) waters. The regression line for bottom waters from the 10 m isobath is drawn from an estimated pre-formed water, where DO equals 4.6 mL L^{-1} (0.21 mmol L^{-1}) and $\delta^{13}C_{DIC}$ equals 0.4‰. The increased slope of 10 m For sub-pycnocline waters, April $\delta^{13}C_{DIC}$ values averaged 0‰ and ranged from -0.4 to 0.3‰;

whereas July's were lower, averaging -1.1‰ and ranging from -2.3 to 0.1‰. Bottom waters along the 20 m isobath exhibited correlations between $\delta^{13}C_{DIC}$ and DO during April and July, and when both months are combined (Table 1: Eqns. 7, 9, 10). No other April waters exhibited such a correlation. During July, $\delta^{13}C_{DIC}$ and DO correlated in middle depth waters (10 m) along the 20 m isobaths (Table 1: Eqn. 11) and in bottom waters on the 10 m isobath (Fig. 6; Table 1: Eqn. 8).

Discussion

Freshwater sources

The salinity, $\delta^{18}O$, and δD of northern GoM waters are dominantly influenced by freshwater discharge from rivers and from evaporation, with precipitation being of very minor importance (Dinnel and Wiseman, 1986). Eighty percent of the discharge delivered to the Gulf of Mexico comes from the Atchafalaya and Mississippi Rivers, and on average, 53% of Mississippi River discharge is transported west of the Mississippi Delta (Etter et al., 2004). Assuming this distribution of river discharge is correct, the Atchafalaya accounts for roughly half of the freshwater on the western shelf. Smaller rivers, such as the Sabine and Brazos, influence Gulf of Mexico seawater at local scales (DiMarco et al., In review).

The $\delta^{18}O$-S and δD-S surface water relationships suggest different sources of freshwater onto the western Louisiana shelf during April and July, the latter when hypoxia is most severe. Isotope data for the Atchafalaya and Mississippi Rivers were collected in 2008 at stations in Melville and St. Francisville, Louisiana, about 100 and

200 km upstream of the respective deltas, by the U.S. Geological Survey (J. Landwehr and T. Coplen, unpubl. data, 2010). These data show April Mississippi $\delta^{18}O$ and δD to be -6.6‰ and -40‰ respectively, while April Atchafalaya River water $\delta^{18}O$ and δD average -5.8‰ and -34‰ respectively; July Mississippi $\delta^{18}O$ and δD average -6.0‰ and -39‰ respectively, and June (no data available for July) Atchafalaya River water $\delta^{18}O$ and δD average -5.5‰ and -34‰ respectively (Coplen, unpublished data). The $\delta^{18}O$-S and δD-S trends observed during April yield y-intercepts (where S = 0) of -6.5‰ and -38‰. These fall between the mixing lines of Atchafalaya and Mississippi River water with GoM seawater, and suggest Mississippi River water is the dominant fresh water influence on the shelf during April. July $\delta^{18}O$ and δD y-intercepts exhibit an increase to -4.7‰ and -28‰ respectively, values more similar to, but higher than the Atchafalaya River water (Table 1, Fig. 4). These data are similar to observations of 2005 salinity and $\delta^{18}O$ in

Louisiana shelf surface waters (Wagner and Slowey, 2011). The Wagner and Slowey S-$\delta^{18}O$ regressions yielded y-intercepts of -6.0 ‰ during May and -4.3‰ in August. Wagner and Slowey acknowledge the difficulty in estimating the fractions of Mississippi and Atchafalaya river waters on the shelf. We attempt a mass balance approach to calculating the respective fractions.

Mass balance calculations of freshwater sources

We use a three-component mass balance mixing model to estimate the relative contributions of Mississippi and Atchafalaya River discharge on the Louisiana shelf. The model is a combination of mass balance equations for salinity

$$S_m = F_{Atch}S_{Atch} + F_{Miss}S_{Miss} + F_{GoM}S_{GoM} \quad (1)$$

and $\delta^{18}O$ (or δD)

$$\delta^{18}O_m = F_{Atch}\delta^{18}O_{Atch} + F_{Miss}\delta^{18}O_{Miss} + F_{GoM}\delta^{18}O_{GoM} \quad (2)$$

where S = salinity, F = Fraction, m = measured, Atch = Atchafalaya, Miss = Mississippi and $F_{Atch} + F_{Miss} + F_{GoM} = 1$. We can assume that $S_{Ath} \approx S_{Miss} \approx 0$ so that $S_m = F_{GoM} S_{GoM}$. These equations combine to yield

$$F_{Atch} = \frac{\delta^{18}O_{Miss} - \frac{S_m}{S_{GoM}}\delta^{18}O_{Miss} + \frac{S_m}{S_{GoM}}\delta^{18}O_{GoM} - \delta^{18}O_m}{\delta^{18}O_{Miss} - \delta^{18}O_{Atch}} \quad (3)$$

For GoM waters we use $S_{GoM} = 36$ and $\delta^{18}O_{GoM} = 1.1‰$ (J. Strauss, unpublished data; Wagner and Slowey, 2011). For these calculations we have only used measurements from stations visited during both April and July (Fig. 1). Using the April Mississippi and Atchafalaya river water $\delta^{18}O$ values within 99% confidence intervals of each correlation (Fig. 4), the model estimates that 53±30% (±1σ) of April surface waters were of Mississippi River origin and 47±30% were from the Atchafalaya River. Substituting surface water δD for $\delta^{18}O$ in equation 3, paired with April river water δD, values yields the unusable results of 40±88% Atchafalaya River water and 60±88% Mississippi River freshwater on the shelf. The high standard deviations of both calculations, especially those based on δD, are associated with values that plot outside of hypothetical mixing zones (Fig. 4). The variability may be the result of changes in the $\delta^{18}O$ and δD of

freshwater discharge related to regional precipitation that is not captured by monthly sampling of upstream waters.

In general, the regressions and mass balance calculations (including error) of April shelf $\delta^{18}O$ and salinity agree with estimates suggesting ≈53% of Mississippi discharge flows west along the inner shelf under the fall to spring circulation pattern (Dinnel and Wiseman, 1986; Etter et al., 2004). The $\delta^{18}O$-S trends for July samples indicate that July freshwater sources are enriched in heavy isotopes compared with April waters (see Fig. 4). Mass balance calculations fail to estimate realistic (i.e., positive) percentages of freshwater sources because measured δD and $\delta^{18}O$ values are higher than those predicted for Atchafalaya and Mississippi River waters at the upstream sampling sites. This may be the result of enhanced summer evaporation of freshwaters within the Atchafalaya basin (i.e. the river and associated wetlands; Van Heerden, 1980), downstream of δD and $\delta^{18}O$ sampling locations (Melville, LA). The high δD and $\delta^{18}O$ of July shelf waters suggest limited Mississippi River influence. Wagner and Slowey (2011) explain similar results as variability in the amount of Red River discharge into the flow of the Atchafalaya River, which would increase its $\delta^{18}O$. These observations (and those made by Wagner and Slowey, 2011) coincide with the timing of the coastal current reversal (Cho et al., 1998), which causes late spring and summer freshwater discharge to pool on the Louisiana shelf and Mississippi discharge to predominantly flow towards the Florida shelf and offshore (DiMarco et al., 2005; Wiseman et al., 1997). Upwelling favorable conditions caused by eastward winds drives the freshwater of the Mississippi River plume off the continental shelf. Thus, the Mississippi River

plume does not contribute to the freshwater distribution seen on the shelf during summers (when eastern winds are dominant). During downwelling favorable conditions (Fall to Spring), the Mississippi River plume remains along the coastline and contributes to the westward (downcoast) flowing Louisiana coastal current (Morey et al., 2003; Nowlin et al., 2005).

Benthic respiration and sources of organic carbon

In the generally accepted hypoxia model (Rabalais et al., 2002b), nutrients fluxed to the shelf by Atchafalaya and Mississippi discharge lead to increased productivity in surface waters in the nearfield particle plume. The consequent flux of labile marine OC below the pycnocline is aerobically respired until a limiting factor is met (either DO or OC). River dominated margins like the Louisiana shelf also flux large contributions of terrestrial OC, and their sediments can act as an important sink for organic carbon (Berner, 1982; Gordon and Goñi, 2004), as well as a source of OC for benthic respiration. Because marine and terrestrial OC have significantly different $\delta^{13}C$ values, -19.5‰ and -26‰ respectively (Sackett, 1964; Hedges and Parker, 1976), carbon isotopes can be used to trace the source(s) of respired OC.

The $\delta^{13}C_{DIC}$ in stratified bottom waters is largely controlled by the $\delta^{13}C$ of pre-formed surface DIC and by aerobic respiration of OC (Fig. 6). Additional processes affecting $\delta^{13}C_{DIC}$ include precipitation and dissolution of carbonate minerals, coastal upwelling, anaerobic respiration, and photosynthesis. Precipitation and dissolution of carbonate minerals have little effect on the $\delta^{13}C$ because of the relatively small fractionation (< 3‰) of the processes (Romanek et al., 1992). Coastal upwelling is

favored during the summer circulation paradigm. The $\delta^{13}C_{DIC}$ and DO of July outer shelf (60 m depth) bottom water (i.e. the water that would be upwelled) average 0.4‰ and 3 mL L^{-1} (Zerai, 2001; J. Strauss, unpubl. data). As DIC concentrations of upwelled waters are likely to be within 10% of pre-formed waters (Aharon et al., 1992), the $\delta^{13}C_{DIC}$ influence of upwelled waters would mostly be masked by aerobic respiration.

Anaerobic oxidation of OC will significantly reduce the $\delta^{13}C_{DIC}$ of anoxic pore waters (McCorkle et al., 1985). Anaerobic respiration in Louisiana shelf sediments is dominated by bacterial reduction of sulfate proximal to the Mississippi River plume (Morse and Rowe, 1999) and the resulting H_2S is quickly mineralized to FeS within the sediments (Lin and Morse, 1991). The CO_2 flux associated with pore water anaerobic respiration into bottom waters averages 39.6 mmol m^2 d^{-1} (Morse and Rowe, 1999). When compared with benthic respiration rates ranging from 5 to 18 mg O_2 m^3 d^{-1} (Dortch et al., 1994), the anaerobic influence on bottom water (lower 2 m) $\delta^{13}C_{DIC}$ would be less than 2%. Marine photosynthesis is associated with a large fractionation factor (~-18‰; Sackett, 1964), and thus would enrich DIC in ^{13}C, increasing the $\delta^{13}C_{DIC}$ and as a consequence the calculated $\delta^{13}C_{Res}$. Aerobic respiration of marine OC generated by photosynthesis would return the light carbon to the DIC pool, thus mainly nullifying its initial effect. Observations in 20 m waters south of Terrebonne Bay suggest that benthic photosynthesis can account for up 23% of DO, but only under periods of consistent calm (Dortch et al., 1994). There are limited estimates of benthic photosynthesis in the turbid inshore waters (i.e. 10 m isobaths) near the Atchafalaya plume. In general, benthic photosynthesis is shown to be light limited inshore (under particle plumes) and nutrient

limited offshore for both Mississippi and Amazon Delta regions (Smith and Demaster, 1996; Lohrenz et al., 1999).

Modeling $\delta^{13}C_{DIC}$-DO trends permits calculation of the respired $\delta^{13}C$ and thus source of respired OC. For example, the complete consumption of DO by aerobic respiration of terrestrial OC (OC_T) yields a lower $\delta^{13}C_{DIC}$ relative to similar consumption of marine OC (OC_M; that is less depleted in ^{13}C). Under these conditions, observation of $\delta^{13}C_{DIC}$ and DO in shelf waters can be incorporated into a closed system mass balance model based on the simplified respiration equation is

$$CH_2O + O_2 \rightarrow CO_2 + H_2O \quad (4)$$

where the amount of CO_2 generated is a 1:1 molar ratio to the amount of O_2 respired. This mass balance equation

$$\delta^{13}C_m = \frac{DIC_{GoM}}{DIC_m}\delta^{13}C_{GoM} + \frac{DIC_{Res}}{DIC_m}\delta^{13}C_{Res} \quad (5)$$

where m = measured and Res = respired. DIC_m is the sum of the initial DIC concentration (DIC_{GoM} = 2.2 mmol L^{-1}) plus the respired DIC added (DIC_{Res}). Assuming aerobic respiration, DIC_{Res} equals the DO consumed (DO_o-DO_m), which is the same as the apparent oxygen utilization (AOU). For DO_o we use 0.2 mmol L^{-1}, which equals isobaths waters is caused by the respiration of more ^{13}C-depleted OC relative to 20-30 m bottom waters.

saturation of DO for the average temperature of shelf waters measured during the July cruise (Weiss, 1970). Equation 5 can now be rewritten:

$$\delta^{13}C_m = \left(\frac{DIC_{GoM}}{DIC_{GoM}+(DO_O-DO_m)} * \delta^{13}C_{GoM}\right) + \left(\frac{(DO_O-DO_m)}{DIC_{GoM}+(DO_O-DO_m)} * \delta^{13}C_{Res}\right) \quad (6)$$

which can then be rewritten to solve for $\delta^{13}C_{Res}$:

$$\delta^{13}C_{Res} = \frac{\delta^{13}C_m[DIC_{GoM}+(DO_O-DO_m) - DIC_{GoM}\delta^{13}C_{GoM}]}{DO_O-DO_m} \quad (7)$$

In waters where salinity indicates mixing with freshwater, its influence can be corrected for using the following mass balances

$$DIC_m = F_{GoM}DIC_{GoM} + F_{Riv}DIC_{Riv} + DIC_{Res} \quad (8)$$

$$\delta^{13}C_m = \frac{F_{GoM}DIC_{GoM}\delta^{13}C_{GoM}+F_{Riv}DIC_{Riv}\delta^{13}C_{Riv}+DIC_{Res}\delta^{13}C_{Res}}{F_{GoM}DIC_{GoM}+F_{Riv}DIC_{Riv}+DIC_{Res}} \quad (9)$$

where salinity is a measure of the fraction of river water present, so that $F_{GoM} = S_m/S_{GoM}$ and $F_{Riv} = 1-(S_m/S_{GoM})$. Thus equations 8 and 9 can be combined into:

$$\delta^{13}C_{GoM-fw} = \delta^{13}C_m - \frac{\delta^{13}C_{Riv}DIC_{Riv}F_{GoM}+\delta^{13}C_{GoM}DIC_{GoM}F_{GoM}}{DIC_{Riv}F_{GoM}+\delta^{13}C_{GoM}F_{GoM}} \quad (10)$$

where the $\delta^{13}C_{GoM-fw}$ is the $\delta^{13}C_m$ corrected for freshwater mixing. The correlation between surface water $\delta^{13}C_{DIC}$ and salinity (Fig. 5) is used to calculate a $\delta^{13}C$ of

freshwater equal to -5.0‰ (Table 1, eq. 6). This $\delta^{13}C_{DIC}$-salinity regression omits four outliers, two of which appear to be either strongly influenced by exchange with atmospheric CO_2 or the result of poorly sealed vials. Additionally, two values offshore of Terrebonne Bay that may be influenced by Mississippi River water are also omitted (Fig. 5). Rivers can be enriched in DIC relative to seawater, and therefore may have an amplified influence on the $\delta^{13}C_{DIC}$ of the seawater-freshwater mixture. DIC concentrations of Mississippi waters are related to discharge rate, with increased discharge correlating with decreased DIC concentration. Summer and fall Mississippi DIC ranges from 2.5 to 3.0 mmol L^{-1}, and spring discharge ranges from 2.2 to 2.5 mmol L^{-1} (Cai, 2003). Additionally, the bicarbonate flux of the Mississippi River has increased by roughly 30% since the beginning of the 20th century due to agricultural practices within the drainage basin (Raymond et al., 2008).

To calculate $\delta^{13}C_{Res}$ in shelf waters that have mixed with river discharge (e.g. salinity between 30 and 34), equations 7 and 10 are combined into

$$\delta^{13}C_{Res} = \frac{\delta^{13}C_m\left[\frac{S_m}{S_{GoM}}DIC_{GoM}+\left(1-\frac{S_m}{S_{GoM}}\right)DIC_{Riv}+(DO_o-DO)\right]-\frac{S_m}{S_{GoM}}\delta^{13}C_{GoM}DIC_{GoM}-\left(1-\frac{S_m}{S_{GoM}}\right)\delta^{13}C_{Riv}DIC_{Riv}}{DO_o-DO_m} \quad (11)$$

where we use a DIC_{Riv} concentration of 3.0 mmol L^{-1}. This value denotes the strongest possible freshwater influence, thus yielding the most conservative estimates of $\delta^{13}C_{Res}$.

DIC_{GoM} is assumed to be 2.2 mmol L^{-1}. Bottom waters along the 10 m isobath and transitional waters were corrected for salinity influence (where salinities range from 30.4 to 35.6). Bottom waters on the 20 m isobath and deeper do not show freshwater influence, so equation 7 was used.

The average $\delta^{13}C_{Res}$ calculated for each zone (e.g., 20+ m bottom, 10 m bottom, and 10 m mid-depth) consists of values within 2σ of the average of all discreet $\delta^{13}C_{Res}$ values within each zone (Table 2). The error assigned to the $\delta^{13}C_{Res}$ calculated for each zone is 1σ of the $\delta^{13}C_{Res}$ values within each depth zone (calculated with outliers removed). The average $\delta^{13}C_{Res}$ calculated for 10 m bottom waters is -25.5±5.7‰. Bottom waters on the 20 m isobaths yield $\delta^{13}C_{Res}$ equal to -17.1±4.7‰. For transitional waters, a large σ prevents determination of $\delta^{13}C_{DIC}$. This is most likely the result of a weak pycnocline (Fig. 2) allowing mixing with oxygenated surface waters at middle depths. Furthermore, these transitional waters may exhibit greater photosynthesis during the day and be respiration-controlled at night (H. Mills, pers. comm., 2010). However, middle depth samples collected at night were non-hypoxic, thus limiting any interpretation.

The $\delta^{13}C_{Res}$ calculated for waters on the 10 m isobath is consistent with the respiration of terrestrial OC sourced from the Atchafalaya Basin (-27 to -23‰; Gordon and Goñi, 2003). There is a 1.8‰ overlap between the error associated with $\delta^{13}C_{Res}$ from 20 m and 10 m isobaths. This overlap, however, it is the result of a single high $\delta^{13}C_{DIC}$

value measured at station 35D. This station is one meter shallower than other stations and may be obscured by incorporation of atmospheric CO_2 through surface water mixing (assuming that river influence is removed through equation 11).

Table 2: 10 m and 20+ m bottom water measurements and calculated $\delta^{13}C_{GoM\text{-}fw}$ and $\delta^{13}C_{Res}$ of July 2008 waters. An asterisk indicates a value excluded from calculation of $\delta^{13}C_{Res}$ (outside 2σ).

Station	Water Depth (m)	Latitude	Longitude	Salinity	$\delta^{13}C_{DIC}$ (‰)	DO (mmol L^{-1})	$\delta^{13}C_{GoM\text{-}fw}$ (‰)	$\delta^{13}C_{Res}$ (‰)
7C	10	29.12 N	91.91 W	33.28	-1.9	0.011	-1.7	-23.4
12C	10	29.06 N	91.77 W	33.57	-1.9	0.003	-1.8	-22.9
4C	10	29.14 N	92.11 W	34.45	-2.3	0.002	-2.4	-29.4
7B	10	28.96 N	90.54 W	35.57	-1.5	0.004	-1.8	-21.3
35D	10	29.30 N	92.46 W	31.21	-1.3	0.093	-0.6	-16.9
BC6	10	29.01 N	91.50 W	33.19	-2.0	0.031	-1.7	-26.4
26D	10	29.58 N	92.90 W	31.62	-2.0	0.083	-1.4	-32.1
30D	10	29.50 N	92.70 W	30.44	-2.5	0.069	-1.7	-34.7
31D	10	29.40 N	92.60 W	31.98	-2.0	0.024	-1.5	-22.3
							Mean	-25.5
							2 SE	1.9
							σ	5.7
8B	17	28.84 N	90.56 W	35.64	-1.6	0.003	*Not Used*	-24.1
33D	18	29.20 N	92.70 W	34.47	-0.9	0.044	-	-19.1
36D	20	29.17 N	92.55 W	34.7	-1.3	0.017	-	-21.5
10B	20	28.62 N	90.55 W	36.14	-0.7	0.077	-	-20.4
13C	20	28.94 N	91.87 W	35.9	-0.8	0.095	-	-25.8
16C	20	28.89 N	91.73 W	35.85	0.0	0.114	-	-11.2
2C	20	29.06 N	92.37 W	35.53	-0.9	0.004	-	-15.2
3B	20	28.58 N	90.78 W	36.27	-0.4	0.033	-	-11.1
5C	20	29.02 N	92.17 W	35.65	-1.0	0.003	-	-16.4
6B	20	28.60 N	90.68 W	36.32	-0.7	0.013	-	-13.5
bc1	20	28.88 N	91.74 W	35.92	-0.7	0.042	-	-16.3
bc10	20	28.60 N	90.89 W	35.23	-0.6	0.044	-	-14.7
bc11	20	28.64 N	91.13 W	-	-1.2	0.030	-	-22.6
bc12	20	28.74 N	91.38 W	-	-0.9	0.015	-	-16.8
bc13	20	28.81 N	91.50 W	35.80	-1.7	0.118	-	-56.7*
bc2	20	28.68 N	91.26 W	-	-1.0	0.012	-	-17.6
bc3	20	28.61 N	91.00 W	35.87	-0.8	0.018	-	-15.2
38d	25	28.90 N	92.75 W	35.71	0.1	0.122	-	-8.6
							Mean	-17.1
							2 SE	2.3
							σ	4.7

Additionally, a T-test shows values from 10 m and 20+ m are statistically different ($p < 0.05$). In general, the higher standard deviation of $\delta^{13}C_{Res}$ values for 10 m bottom waters is due to the more variable environment and reliance on three different measurements (salinity, $\delta^{13}C_{DIC}$, and DO), whereas calculations of $\delta^{13}C_{Res}$ for 20 m bottom waters do not rely on salinity. Furthermore, of the aforementioned quantities, $\delta^{13}C_{DIC}$ and DO are the most volatile as they can be affected by atmospheric exchange, productivity, and mixing. The precision of the $\delta^{13}C_{DIC}$ measurement (~0.1‰) translates to an average $\delta^{13}C_{Res}$ error of ±1.5‰ for 10 m depth, salinity-corrected samples and 1.6‰ for 20 m depth samples.

In general, OC_T is delivered to the shelf as dissolved and particulate OC (DOC and POC) and as OC attached to suspended sediments (Gordon and Goñi, 2003; Bianchi et al., 2007). The $\delta^{13}C$ composition of OC_T flux is dependent on the dominant plant source (i.e. C3 vs C4 plants), so that OC composed of grassy particles (C4) yields higher $\delta^{13}C$ values (>-20‰) than that composed of woody particles (C3; <-21‰). Additionally, algal material supply additional high-$\delta^{13}C$ OC (in the form of dissolved organic carbon) to the shelf (Bianchi et al., 2004). The OC_T flux from the Atchafalaya River to the shelf is composed of non-woody grass-like sources and woody materials. Hydrodynamic sorting associates heavier woody particles with sands and finer grassy particles with muds and silts (Bianchi et al., 2007), thus C3-derived materials are deposited inshore relative to finer C4-derived particles. Furthermore, labile C3-derived OC_T ($\delta^{13}C$ = -27‰) are carried by the Atchafalaya River and delivered to bottom waters and surficial sediments along and inshore of the 10 m isobath (Gordon and Goñi, 2003). The 10 m

isobath falls within Atchafalaya Bay and is thus within the aforementioned zone of OC_T influence. The flux of labile POC from Louisiana's coastal wetlands and bays onto shelf waters through event driven and tidal processes can support microbial communities in the benthos (Dagg et al., 2008) and generally settles near shore in shallow depths (Green et al., 2006; Trefry et al., 1994). This OC_T may account for the low $\delta^{13}C_{Res}$ of -26±4‰ observed near the mouth of Terrebonne Bay at station 7B.

The relatively high $\delta^{13}C_{Res}$ of -17.6±4.7‰ calculated for bottom waters in depths of 20 m and greater suggests that algal, marine or C4 associated OC (-20 to -18‰) is being predominantly respired at these depths (Hedges and Parker, 1976; Bianchi et al., 2004; 2007). This finding correlates with a seaward decline in terrestrial OC, and may be the result of either fallout or complete respiration of suspended OC_T beyond the 10 m isobaths (Gordon and Goñi, 2003; 2004; H. Mills, personal comm. 2010). Furthermore, the respiration of terrestrial OC may be continuing in the mid-depth waters along the 20 m isobath, where respiration is indicated by DO-$\delta^{13}C$ correlation and low DO levels (Figs. 2, 5). Under this scenario, the OC fallout from middle-depth waters would be of marine origin and would account for the marine $\delta^{13}C_{Res}$ signal in bottom depths of 20 m and deeper. Additionally, the $\delta^{18}O$ and δD of surface waters do not identify Mississippi River discharge on the shelf during summers. Therefore the OC or nutrients that are sustaining shelf hypoxia west of Terrebonne Bay is entirely of Atchafalaya origin. Rabalais et al. (2002a) argues that the contribution of organic carbon from the Mississippi and Atchafalaya rivers is inconsequential, owing to its reduced volume comparative to OC generated by shelf productivity, and difficulty in being transported to

the shelf. More recently, a budget for the Louisiana shelf by Green et al. (2006) indicates that terrestrial OC can supply 23% of the OC demand of the hypoxic zone. We provide evidence that the dominant OC being respired in bottom waters along the 10 m isobaths of the western Louisiana shelf (proximal to Atchafalaya Bay) is terrestrial-sourced.

Conclusions

Using stable isotopes of oxygen and hydrogen we have shown April 2008 Louisiana shelf waters are influenced by both Atchafalaya and Mississippi river discharge. Values of July waters are too high to be explained by mixing with unmodified Mississippi or Atchafalaya waters. The high isotopic compositions of shelf surface water relative to salinity, coinciding with the reversal of the Louisiana coastal current, provides qualitative evidence that Atchafalaya River water is the dominant freshwater source during July on the continental shelf off Terrebonne and Atchafalaya Bays.

Carbon isotopes of DIC correlate with DO in bottom and middle depth waters and can correlate with salinity in surface waters. Using mass balance calculations, we have provided quantitative estimates for the carbon isotope compositions of respired carbon in bottom waters. Middle depth waters indicate significant water column respiration near the pycnocline, however the $\delta^{13}C$ of respired carbon could not be calculated, likely owing to reoxygenation from mixing of surface waters. Nevertheless, these data justify the importance of water column respiration as a component of hypoxia formation. Bottom waters indicate that terrestrially-derived organic carbon is

dominantly respired in inshore waters of 10 m depth, and that marine organic carbon is dominantly respired at depths of 20 m and greater. These calculations correspond to inshore delivery of labile OC by the Atchafalaya Basin and tidal fluxes which both exhibit a seaward decline. These data show that while the tenets of the general hypoxia model are true, the influence of terrestrial OC cannot be overlooked, especially at shallower depths.

CHAPTER III

STABLE ISOTOPES IN MOLLUSK SHELLS AS INDICATORS OF BENTHIC RESPIRATION AND FRESH WATER INFLUENCE AND PENETRATION ON THE TEXAS-LOUISIANA SHELF

Overview

To investigate the potential for mollusks as proxies for benthic respiration and hypoxia in the northern Gulf of Mexico, five gastropods (*Conus austini* and *Strombus alatus*) and five bivalve (*Pteria colymbus* and *Spondylus calcifer*) shells, representing six unique Texas-Louisiana shelf localities and three collection periods from 1965-2009, were sequentially analyzed for oxygen and carbon stable isotopes ($\delta^{18}O$ and $\delta^{13}C$). Mollusk $\delta^{18}O$ and $\delta^{13}C$ were compared with new and previously published isotopic measurements of shelf waters. Analyses of the $\delta^{13}C$ of dissolved inorganic carbon (DIC) of Texas shelf bottom waters reveal a significant positive correlation with bottom water dissolved oxygen (DO). Louisiana shelf surface water $\delta^{13}C_{DIC}$ and $\delta^{18}O$ values indicate significant fresh water influence (i.e. values below 2 ‰), whereas bottom waters are more similar to open ocean Gulf of Mexico values. Coastal *S. alatus* $\delta^{18}O$ and $\delta^{13}C$ are heavily influenced by fresh water, suggesting the 7 m collection depth was consistently mixed with low salinity and low $\delta^{18}O$ surface waters. *Conus austini* collected from 24 m traces a low salinity event related to the arrival of hurricane Camille in 1969, which *C. austini* from 30 m depth do not strongly record. $\delta^{13}C$ values of 1972 Louisiana shelf *C. austini* specimens are up to 1.5 ‰ higher than modern Gulf of Mexico *C. ermineus* $\delta^{13}C$,

indicating a $\delta^{13}C_{DIC}$ reduction during the last four decades associated with intrusion of ^{13}C-depleted fossil fuel CO_2. Summer $\delta^{13}C$ reductions in Texas shelf *P. colymbus* shells imply DO was reduced by ≈0.7 ml L^{-1}, indicating near-hypoxic waters comparable to contemporaneous observations during NOAA SEAMAP cruises. Louisiana shelf *C. austini* do not exhibit the seasonal $\delta^{13}C$ declines observed in the modern Louisiana hypoxic zone, suggesting limited or no hypoxia off Terrebonne Bay between 24 and 30 m.

Introduction

Hypoxia, the depletion of dissolved oxygen (DO) below 1.4 mL L^{-1}, is a serious environmental concern in the northern Gulf of Mexico (GoM). Northern GoM hypoxia was first documented on the Louisiana shelf in 1972 (Ward and Stanford, 1979). The first comprehensive spatial surveys of shelf hypoxia were performed in 1975 and 1976 (Turner and Allen, 1982) and have been performed annually since the 1980s (Rabalais et al., 2002a). There is a link between Texas and Louisiana shelf hypoxia and Mississippi and Atchafalaya river discharge, which induces stratification in and delivers nutrients to shelf waters (Rabalais et al., 2002b). The stratification is exacerbated by the lower wind stress and a reversal of coastal current during summers (Dinnel and Wiseman, 1986; Nowlin et al., 2005). Hypoxia on the middle Texas shelf was first measured off Freeport by Harper et al. (1981) during the summer of 1979 and was interpreted to be the result of a diatom bloom caused by above-average discharge from the Brazos River. A

subsequent middle Texas shelf hypoxic event has been chemically linked to Brazos River discharge (J. Strauss, unpubl. data).

Because comprehensive surveys of GoM hypoxia have all taken place after the heavy anthropogenic modification of the Mississippi and Atchafalaya River system, understanding the natural influence on GoM hypoxia requires proxy records. Long-term records derived from foraminiferal abundances have suggested a strong increase in hypoxia during the middle of the 20th century (Osterman, 2003; Osterman et al., 2008; 2009). These records, while valuable, do not have the resolution to capture conditions on an annual scale.

Oxygen and carbon stable isotope ratios ($\delta^{18}O$ and $\delta^{13}C$) in marine mollusk shells have been successfully used as high resolution proxies for ocean temperature, salinity, and environmental conditions (Andreasson et al., 1999; Goodwin et al., 2003; Ivany et al., 2003; Surge et al., 2003).When sequentially analyzed, mollusk shells can yield records spanning over 100 years (Schöne et al., 2005). Furthermore, shelled mollusks occupy tropical, temperate and polar seas from shelf to abyssal depths.

Chapter II shows have shown that $\delta^{13}C$ of dissolved inorganic carbon (DIC), the carbon pool from which mollusks precipitate their shells, correlates with dissolved oxygen concentrations in Louisiana shelf bottom waters. Here we examine of stable isotope records in mollusk shells as proxies for GoM hypoxia, using $\delta^{18}O$ for temperature seasonality and sclerochronology and $\delta^{13}C$ as an indicator of bottom water respiration (i.e. remineralization of organic carbon) and hypoxia. Additionally, mollusk shell $\delta^{18}O$ and $\delta^{13}C$ can be used to indicate fresh water influence on bottom waters, and

thus provide evidence for water column mixing which inhibits stratification, a requirement for hypoxia formation (Wiseman et al., 1997).

In addition to mollusk data, we present unpublished data on Texas shelf $\delta^{13}C_{DIC}$ to complement published $\delta^{18}O$ data for the Texas shelf and $\delta^{18}O$ and $\delta^{13}C$ data for the Louisiana shelf (J. Strauss, unpubl. data; Chapter II).

Methods

Study area, field sampling, and samples

For this study we have chosen five bivalve and five gastropod shells collected from six localities on the Texas-Louisiana shelf (Table 3), concentrating on two hypoxia-susceptible localities. On the Texas shelf, we collected mollusk shells from offshore Freeport, where summer hypoxia has been measured sporadically in the past (Harper et al., 1981; NOAA SEAMAP). Hypoxia at this locality in 2007 was found to be induced by above-average discharge of the Brazos River, while during 2008 hypoxia was traced to Mississippi-Atchafalaya River discharge (J. Strauss, unpubl. data). On the Louisiana shelf, we have chosen two localities subject to recurrent seasonal hypoxia that are now routinely monitored (Rabalais et al., 2002b). One offshore and two coastal Louisiana shelf sites have also been included in this study to provide baseline data for outer shelf and nearshore environments (2578, 2712 and Sc-1 on Fig. 7).

It is especially difficult to collect living mollusk shells from the turbid waters and sandy-silty substrates of the Texas and Louisiana shelves, where shrimp trawling

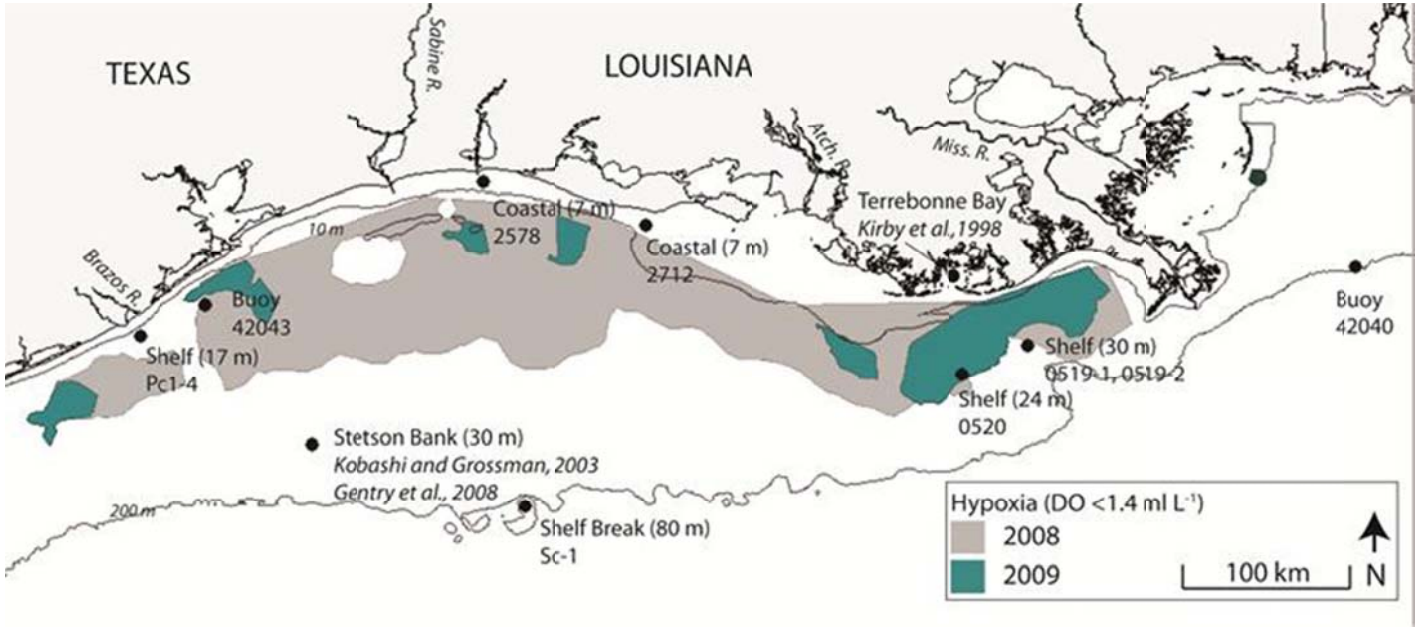

Figure 7: Map of shell collection localities on the Texas-Louisiana shelf. Dark grey shading represents the spatial extent of 2009 hypoxia; light grey shading reveals widespread 2008 hypoxia.

Table 3: Sample locations, collection dates, species, and isotopic values.

Sample number	Sample location	Collection Date	Latitude (degrees)	Longitude (degrees)	Depth (m)	Taxon	Length (mm)	Min. $\delta^{18}O$ (‰)	Max. $\delta^{18}O$ (‰)	Mean $\delta^{18}O$ (‰)	Min. $\delta^{13}C$ (‰)	Max. $\delta^{13}C$ (‰)	Mean $\delta^{13}C$ (‰)
0519-1	LA shelf	2/6/1972	28.75 N	90.12 W	30	*Conus austini*	38	-1.0	1.0	0.2	1.5	2.6	2.0
0519-2	LA shelf	2/6/1972	28.75 N	90.12 W	30	*Conus austini*	39	-1.1	1.0	0.1	1.6	2.8	2.2
520	LA shelf	2/6/1972	28.58 N	90.50 W	24	*Conus austini*	41	-1.4	0.8	-0.3	1.3	2.4	1.8
2712	LA nearshore	7/13/1964	29.45 N	92.35 W	7	*Strombus alatus*	58	-2.1	-1.0	-1.6	-2.5	-0.9	-1.6
2578	LA nearshore	4/1/1965	29.70 N	93.30 W	7	*Strombus alatus*	65	-1.8	-0.4	-1.2	-1.6	0.1	-0.7
Sc-1	LA shelf break	8/22/2008	27.81 N	93.06 W	80	*Spondylus calcifer*	184	-0.5	1.2	0.7	-0.7	1.6	0.2
Pc-1	TX shelf	11/6/2009	28.80 N	95.30 W	17	*Pteria colymbus*	55	-1.3	1.7	0.0	0.0	1.2	0.6
Pc-2	TX shelf	11/6/2009	28.80 N	95.30 W	17	*Pteria colymbus*	47	-1.4	0.8	-0.2	-0.4	1.1	0.1
Pc-3	TX shelf	11/6/2009	28.80 N	95.30 W	17	*Pteria colymbus*	45	-1.2	1.1	-0.4	-0.2	1.7	0.4
Pc-4	TX shelf	11/6/2009	28.80 N	95.30 W	17	*Pteria colymbus*	49	-1.4	1.3	-0.3	0.5	1.7	1.1

prevents settlement and threatens survivorship of larger epibenthic mollusks (G. Rowe, personal comm., 2009). Due to these difficulties, for all but two localities (Texas shelf and Louisiana outer shelf) we have relied on historic collections provided by the Texas Cooperative Wildlife Collection (TCWC).

Samples from the middle Texas shelf include four specimens of *Pteria colymbus* (Pc-1 to Pc-4) that were collected on November 6th, 2009 by trailing an oyster dredge over a slightly rocky bottom (Fig. 7). *Pteria colymbus* is a bivalve found in the mid-southern Texas coast and is endemic to the Carolinian and Caribbean molluscan provinces (Andrews, 1971). It inhabits coastal reefs and structures where it attaches to gorgonians and filter feeds (Tunnell et al., 2010). Its shell is composed of a prismatic aragonite outer layer and nacreous aragonite inner layer (Epstein and Lowenstam, 1953; Lowenstam, 1954). Epstein and Lowenstam (1953) found that temperatures calculated from *P. colymbus* shell $\delta^{18}O$ agreed with instrumentally measured seasonal ranges. Beyond the 1953 study, we know of no known published stable isotope work on this species.

A single specimen of *Spondylus calcifer* was collected by dredge from a rocky bottom on the Louisiana shelf break (80 m depth) during a cruise of opportunity aboard the R/V Pelican. *Spondylus* shells are composed of a thick calcitic inner layer and thin aragonitic outer layer. They are epibenthic, cementing their shells to boulders, corals or other hard substrates in reef environments at depths up to 100 m (Abbot, 1974). This site has been included to provide a record of offshore marine conditions.

Additional samples were provided by the TCWC. These gastropod specimens were collected during the 1960s and 1970s, when mollusk populations were less affected by trawling. Included are two specimens of *Strombus alatus* (2578 and 2712) collected from two localities on the inshore western Louisiana coast in 1964 and 1965. *Strombus alatus* are closely related to the Caribbean *S. pugilis*, which were analyzed for stable isotopes by Geary et al. (1992). They yielded isotopic records of about two years, with $\delta^{13}C$ appearing to track $\delta^{13}C_{DIC}$. *Strombus alatus* are herbivorous gastropods that generally occupy sandy to muddy substrates. They are also known to thrive in euryhaline environments such as estuaries and bays (Abbot, 1974). In addition to *Strombus,* we have also analyzed three specimens of *Conus austini* (0519-1, 0519-2, and 0520) collected in 1972 from two nearby localities on the Louisiana shelf, where hypoxia is prominent today. *Conus* are carnivorous gastropods that feed on specific prey, either other mollusks, polychaete worms and in some cases fishes (Kohn, 1994). Modern and fossil *Conus* shells have yielded multi-year isotopic and trace element records spanning up to 8 years (Kobashi and Grossman, 2003; Gentry et al., 2008). All of the chosen mollusks are epibenthic, so that their shell chemistry will be less influenced by pore waters, where anaerobic respiration heavily influences $\delta^{13}C_{DIC}$ (McCorkle et al., 1985).

Bottom water samples have been collected off the Texas-Louisiana shelf during cruises in April and July, 2008. Data for temperature, salinity, DO, $\delta^{18}O$, and $\delta^{13}C_{DIC}$ are reported in Chapter II except for new $\delta^{13}C_{DIC}$ data of the Texas shelf. These sample localities are shown in Appendix 1. These measurements provide environmental data for mollusk growth and serve as an indication of bottom water respiration (Chapter II).

Measured temperature data are supplemented by data from NOAA buoys 42040 (29.21° N, 88.21° W) and 42043 (28.98° N, 94.92° W).

Shell preparation and sample treatment

To prepare shells for isotopic sampling, modern specimens were first soaked in 6% NaClO to remove the periostracum. The sampling surface was then lightly scrubbed with 30% hydrogen peroxide to remove any remaining organic material, thoroughly rinsed with distilled-deionized water and dried at 40°C. Shells were sampled for isotopic analysis using a dental drill at low speeds with a 0.8 mm carbide dental bur. For each shell, ~300 μg powder samples were taken along the axis of shell growth (Fig. 8). Sampling adhered to methods described by Wefer and Berger (1991), with special care being taken not to penetrate the inner layers of shell, which may have a different isotopic composition. *Pteria colymbus* specimens were sampled on the shell exterior, whereas the *Spondylus* specimen was sectioned with a rock saw along its growth direction and sampled on the interior. Gastropods were sampled close to the shoulder structure following the spiral growth. Kobashi and Grossman (2003) demonstrated that isotopic concentrations exhibit little or no variation from the shoulder towards the siphonal canal in *Conus* gastropods.

Analytical methods

One hundred to 150 μg of $CaCO_3$ powder was digested in nearly pure orthophosphoric acid (specific gravity 1.91-1.93) at 70°C and the evolved CO_2 was

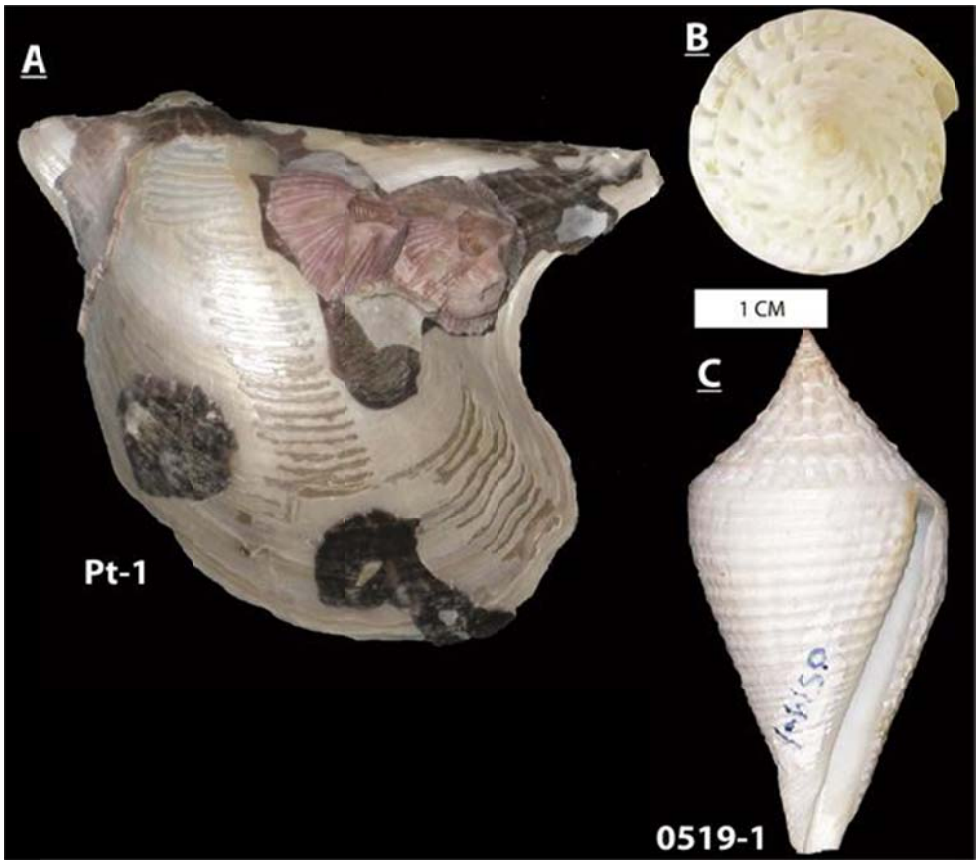

Figure 8: Sampling strategies for *Conus austini* (0519-1) and *Pteria colymbus* (Pt-1) bivalve shells. **A.** The outer aragonitic shell layer of *Pteria* specimens were milled without sectioning the shell so that samples of adequate weight could be acquired. Barnacles and oysters attached to the shell surface presented obstacles in sampling the longest growth axes. **B.** View of apex of *C. austini* where milled sample sites are visible. **C.** Lateral view of *C. austini* with mill locations visible on the shell spire.

analyzed on a Thermo Finnigan DeltaPlus XP isotope ratio mass spectrometer attached to a Thermo Finnigan Gasbench II gas handling device at Stable Isotope Geoscience Facility (SIGF) in the College of Geosciences, Texas A&M University. Oxygen and carbon isotopic ratios were calibrated to the Vienna Peedee Belemnite standard (VPDB) using NBS-19 reference material ($\delta^{18}O$ = -2.20‰, $\delta^{13}C$ = 1.95‰). Analytical precision for all samples was ±0.1‰ for $\delta^{18}O$ and ±0.06‰ for $\delta^{13}C$.

Water samples were analyzed for $\delta^{13}C_{DIC}$ by acidifying 500 µL aliquots of seawater with 50 µL of phosphoric acid in an airtight exetainer vial flushed with ultra-high purity He (Torres et al., 2005). The evolved headspace CO_2 was analyzed on a Thermo Finnigan DeltaPlusXP Isotope Ratio Mass Spectrometer attached to a GasBench II automated gas preparation and delivery system in the SIGF. $\delta^{13}C_{DIC}$ measurements was standardized using NBS-19 reference material ($\delta^{13}C$ = 1.95). Precision of $\delta^{13}C_{DIC}$ measurements was verified using an internal $NaHCO_3$ solution. The precision of this reference solution were at or better than 0.08‰.

Results

Carbon isotopes of Texas shelf waters

Twenty $\delta^{13}C_{DIC}$ values of 2007 Texas shelf surface waters range from -1.0 to 0.1‰ and average -0.3±0.3‰. Twelve bottom water samples exhibit slightly higher values ranging from -0.6 to 1.1‰ and averaging 0.1±0.5‰ (Fig. 9). Surface water $\delta^{13}C_{DIC}$ do not exhibit any correlations with depth, salinity or $\delta^{18}O$. Bottom water $\delta^{13}C_{DIC}$ are higher at increased depths, and do exhibit a weak correlation with salinity (r^2

= 0.30) and a stronger correlation with DO ($r^2 = 0.60$) (data from DiMarco et al., submitted).

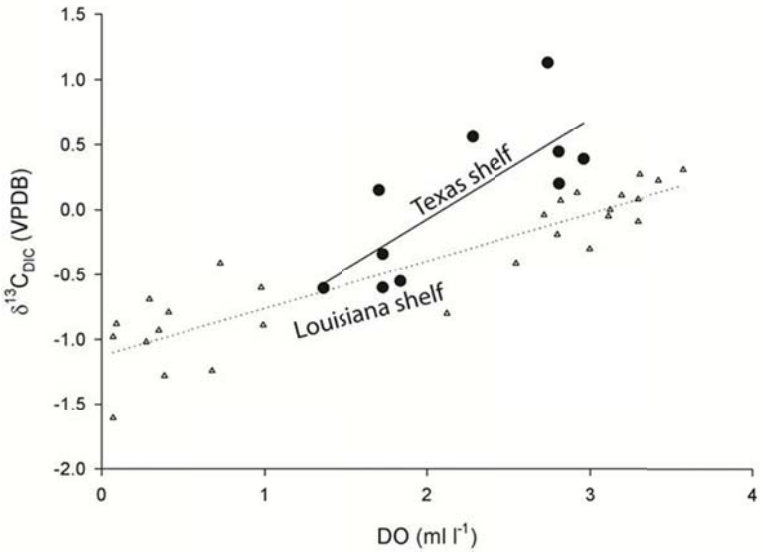

Figure 9: DO- $\delta^{13}C_{DIC}$ correlations of Texas (this study) and Louisiana shelf bottom waters (Chapter II). The correlations track the influence of respiration of ^{13}C-depleted organic carbon.

Mollusk stable isotopes

Table 3 lists the ranges, medians and averages of $\delta^{18}O$ and $\delta^{13}C$ for each sampled shell. Figures 10 and 11 illustrate an XY plot and box-and-whisker diagram of stable isotope results from this study as well as results for *C. ermineus* from the Stetson Bank (Kobashi and Grossman, 2003; Gentry et al., 2008) and *Crassostrea gigas* from Terrebonne Bay (Kirby et al., 1998).

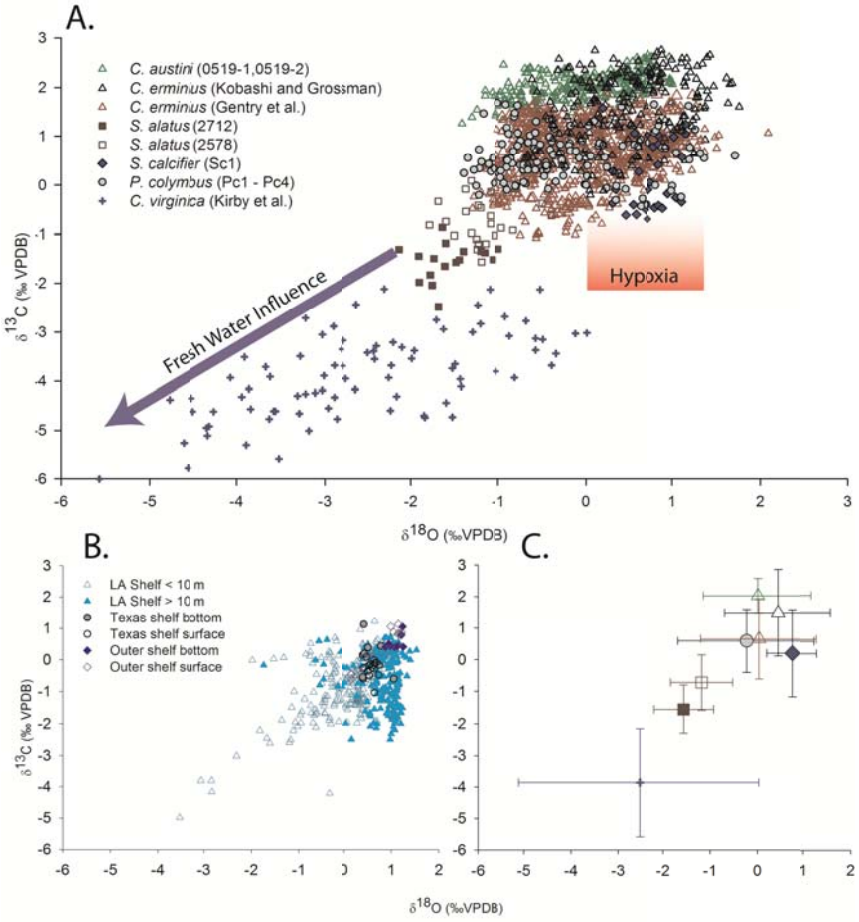

Figure 10: A. XY plot of GoM mollusk shell $\delta^{13}C$ and $\delta^{18}O$ values from this and other studies. Values that plot in negative $\delta^{13}C$ and $\delta^{18}O$ space are indicative of fresh water influence, as indicated by the arrow. The isotopic region of hypoxia is defined as the $\delta^{13}C_{DIC}$ values where DO is less than 1.4 ml L^{-1} for 2007 Texas and 2008 Louisiana shelf waters (Chapter II), as calculated from equations 12 and 13, and the equilibrium $\delta^{18}O$ of aragonite (Grossman and Ku, 1986) for temperatures ranging from 25 to 30°C (using $\delta^{18}O_{sw}$ = 1.1‰). **B.** Plot of shelf $\delta^{18}O$ and $\delta^{13}C_{DIC}$ reported from this study, from Chapter II and from unpublished data (J. Strauss). Note the correlation of $\delta^{13}C$ and $\delta^{18}O$ in surface waters caused by fresh water influence. **C.** Plot of isotopic means for individual and/or groups of shells. The symbols are the same as Figure 10A. Error bars represent 2σ.

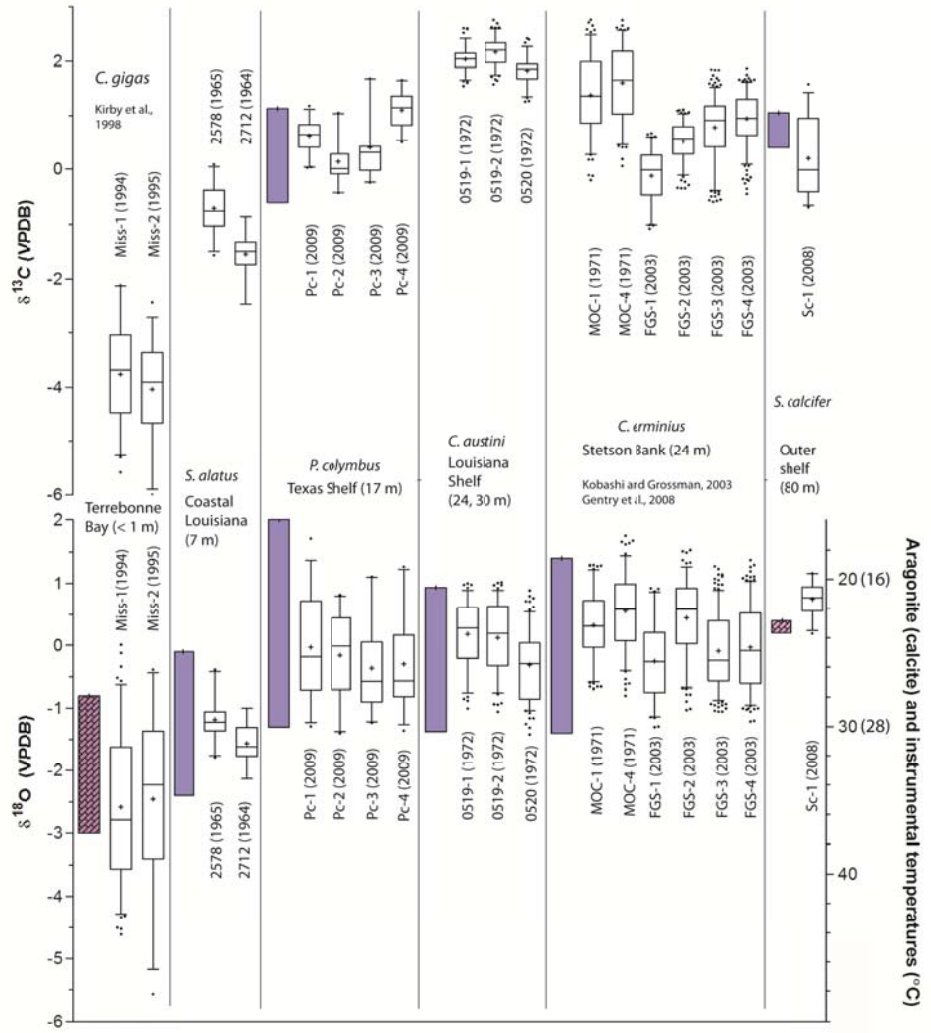

Figure 11: Box and whisker plot of $\delta^{13}C$ and $\delta^{18}O$ of shells sampled for this study and additional *C. ermineus* from the Stetson Bank (Kobashi and Grossman, 2003; Gentry et al., 2008) and *C. gigas* from Terrebonne Bay (Kirby et al., 1998). Where available, $\delta^{13}C_{DIC}$ values are given for the collection localities (shaded boxes). For the $\delta^{18}O$ diagram, an aragonite and calcite temperature scale is shown using relations from Grossman and Ku (1986) and Kim and O'Neil (1997) with a $\delta^{18}O_{sw}$ of 1.1 ‰. Calcite temperatures are in parentheses. Also shown are seasonal ranges of equilibrium aragonite (shaded boxes) and calcite (stippled boxes) $\delta^{18}O$.

Louisiana shelf *Conus austini* specimen 0519-1 was sampled 98 times from the apex to the shell margin. The shell yields $\delta^{18}O$ values ranging from -1.0 to 1.0‰ and averaging 0.2±0.5‰. $\delta^{13}C$ values of 0519-1 average 2.0±0.2‰ and range from 1.5 to 2.6‰. Specimen 0519-2, collected from the same dredge haul as 0519-1, was sampled 105 times. It exhibits $\delta^{18}O$ values essentially identical to 0519-1, ranging from -1.1 to 1.0‰ with an average 0.1±0.5‰. $\delta^{13}C$ values of 0519-2 range from 1.6 to 2.7‰ and average 2.2±0.3‰, similar to 0519-1 data. Shell 0520, collected at slightly shallower depths, was sampled 74 times. The $\delta^{18}O$ values of specimen 0520 are slightly lower than the 0519 shells, and range from -1.4 to 0.8‰ with an average of -0.3±0.6‰. $\delta^{13}C$ values of 0520 average 1.8±0.2‰ and range from 1.3 to 2.3‰.

The $\delta^{18}O$ and $\delta^{13}C$ of Louisiana inner shelf *S. alatus* shells are lower relative to other sampled shells by 1 to 2‰ and 2 to 3‰ respectively. Shell 2712 yielded 17 samples with $\delta^{18}O$ ranging from -2.1‰ to -1.0‰ and averaging -1.6±0.3‰. Its $\delta^{13}C$ values range from -2.5 to -0.9‰ and average -1.6±0.4‰. Shell 2578 was sampled 24 times and yielded $\delta^{18}O$ values ranging from -1.8 to -0.4‰ and averaging -1.2±0.3‰. $\delta^{13}C$ values of 2578 range from -1.6 to 0.1‰ and average -0.7±0.4‰.

The *S. calcifer* from the Louisiana shelf break (Sc-1) was sampled 28 times, yielding a $\delta^{18}O$ range of 0.2‰ to 1.2‰ and an average value of 0.7±0.3‰. Sc-1 $\delta^{13}C$ values range from -0.7 to 1.6 ‰ and average 0.2±0.7‰. Sc-1 shows the highest average $\delta^{18}O$ of all specimens sampled.

Stable isotopes of Texas shelf *P. colymbus* specimens 1-4 (Pc1 – Pc4) show $\delta^{18}O$ values that range from -1.4 to 1.7‰ and average -0.2‰. Mean values from

individual shells are within 0.4‰ of each other, and minima are within 0.2‰. Pc-1 exhibits a high $\delta^{18}O$ value of 1.7 ‰ that exceeds maxima of the other Pc shells by at least 0.4‰. Average $\delta^{13}C$ values for Pc1-4 vary, with Pc2 yielding the lowest mean of 0.1‰ and the Pc-4 exhibiting the highest mean of 1.1‰. The minima and extrema are also considerably variable (Table 3).

Discussion

Texas-Louisiana (TX-LA) shelf waters

Water temperatures on the TX-LA shelf generally exhibit a seasonality of 10 to 14°C, ranging from 16 or 20 to 30°C (NOAA NDBC Buoys 40430 and 40434). No significant day to night temperature shifts have been observed by buoys or in water column profiles (S. DiMarco, unpubl. data, 2008). Outer Texas and Louisiana shelf bottom waters (80-100 m) exhibit limited seasonality of about 2°C with temperatures of 19 to 21°C (Antonov et al., 2010; Locarnini et al., 2010).

Typical hypoxic waters on the TX-LA shelf are more coastal, often at or under 30 m depth, and are strongly influenced by freshwater discharge (Rabalais et al., 2002a). Chapter II present oxygen isotope data to trace freshwater sources on the Texas and Louisiana shelves. We use these data in along with unpublished data (J. Strauss) to characterize the oxygen isotopic composition of Texas-Louisiana shelf waters. In general, inner Louisiana shelf and coastal surface waters show strongly depleted $\delta^{18}O$ and $\delta^{13}C_{DIC}$ values (i.e., <-2‰) that covary with salinity due to the influence of Mississippi and Atchafalaya discharge (Fig. 10). Texas shelf waters do not exhibit as

much fresh water influence. The Mississippi and Atchafalaya Rivers account for the majority of fresh water (> 80%) into the Gulf of Mexico, with the remainder of freshwater fluxed from smaller rivers at more regional scales (e.g., the Brazos River). The $\delta^{18}O$ of Mississippi and Atchafalaya discharge range from -7 to -4‰ (Lee and Veizer, 2003). Rivers with more southern drainage basins exhibit higher $\delta^{18}O$ values due to Rayleigh distillation of cloud moisture over the continental landmass (Dutton et al., 2005); for example, Brazos River water annually averages -2.7‰ (B.K. Coffman and E. Grossman, unpubl. data, 2010). Thus, shelf waters influenced by the Brazos River would maintain higher (more marine) $\delta^{18}O$ values than Louisiana shelf waters of the same salinity. The influence of river discharge on the $\delta^{13}C_{DIC}$ of shelf waters is a consequence of the river water DIC concentration and its $\delta^{13}C$. Open ocean DIC values are generally 2.2 mmol L^{-1}, whereas river DIC values can be higher; for example, Mississippi discharge has been measured to range from 2.5 to 3.0 mmol L^{-1}(Cai, 2003; Raymond et al., 2008). Additionally, river water $\delta^{13}C_{DIC}$ is usually strongly depleted in ^{13}C due to the influence of oxidized biogenic carbon (Drever, 1997). Using the relationship between coastal salinity and $\delta^{13}C_{DIC}$, in Chapter II Mississippi-Atchafalaya $\delta^{13}C_{DIC}$ was calculated to average -5‰. Brazos River $\delta^{13}C_{DIC}$ has been measured at -6.7‰ in Bryan, TX (J. Strauss, unpubl. data, 2010).

The isotopic composition of bottom water on the TX-LA shelf depends on freshwater input, depth, and degree of stratification. Typical shelf bottom waters at depths greater than 10 m are usually chemically similar to open ocean GoM values (Fig. 10), with salinity >35, $\delta^{18}O \approx 1‰$ and $\delta^{13}C = 0\text{-}1‰$. In contrast, bottom waters above 10 m exhibit low $\delta^{18}O$ and $\delta^{13}C$ from freshwater influence. Under hypoxic conditions, $\delta^{13}C_{DIC}$ of bottom waters are lowered by respiration of organic carbon (OC), yielding a positive correlation between DO and $\delta^{13}C_{DIC}$. The relationship for waters from the Texas (July, 2007; this study) and Louisiana (Chapter II) shelves are respectively

$$\delta^{13}C_{DIC} = 0.77(\pm 0.22)\cdot DO - 1.6\ (\pm 0.5)\ \ (R^2 = 0.60) \qquad (12)$$

and

$$\delta^{13}C_{DIC} = 0.37(\pm 0.03)\cdot DO - 1.1\ (\pm 0.08)\ (R^2 = 0.82) \qquad (13)$$

where the higher correlation coefficient for Louisiana shelf data is due to a greater number of samples, stronger stratification, and more widespread hypoxia on the Louisiana shelf. Thus, hypoxic waters on the Texas shelf are indicated by $\delta^{13}C_{DIC}$ values below 0.5‰ on the Texas shelf and -0.6‰ on the Louisiana shelf.

Bottom waters can be susceptible to coastal upwelling, which is prevalent under summer coastal circulation (Li et al., 1997), and to the flux of CO_2 generated through pore-water respiration (both aerobic and anaerobic) (Lin and Morse, 1991). At depths greater than 10 m, upwelling would introduce oxygen-bearing waters from offshore to the study localities. Observations of offshore waters during August 1994 by Zerai (2001)

and Jochens (1998) show water upwelled onto the TX-LA shelf from 60 m depth would exhibit a $\delta^{13}C_{DIC}$ between roughly -0.4 and -0.9‰ and have a DO of 3.0 to 3.3 ml L^{-1}. The upwelled waters on the TX-LA shelf are close in $\delta^{13}C_{DIC}$ and DO concentration to pre-hypoxic bottom waters. Thus, the effect of upwelled waters (i.e. introduction of new DIC and DO) would be limited by subsequent respiration, which would follow the relationships described by equations 12 and 13. Lower $\delta^{13}C_{DIC}$ values reported for the Texas shelf (-0.9‰) are lower than values of oxygenated coastal waters, and therefor may lead to a false interpretation of hypoxia if significant upwelling were to occur.

Finally, CO_2 generated by anaerobic respiration in pore waters can contribute to bottom water $\delta^{13}C_{DIC}$. We believe such influence is minimal, as the average CO_2 flux of 39.6 mmol m^2 d^{-1} associated with pore water anaerobic respiration into bottom waters (Morse and Rowe, 1999) is dwarfed by the aerobic bottom water (lower 2 m) respiration rates (Dortch et al., 1994). Harper et al. (1981) report H_2S odor detected in bottom waters by divers (i.e. in the waters that breached the diver's mask), but we reason that SCUBA diver activity likely dispersed upper sediments and their pore waters.

Mollusk shell stable isotopes

Oxygen isotopes and isotopic temperatures

In general, the $\delta^{18}O$ ranges of Texas and Louisiana shelf shells (*Pteria* and *Conus*) are similar, with ranges overlapping with each other and with previously published values (Fig. 11). The $\delta^{18}O$ values of coastal *S. alatus* shells (2578, 2712) are lower by 1 to 2‰ relative to other aragonitic shells, yielding $\delta^{18}O$ ranges that fall between estuarine *C. gigas* shells (Kirby et al., 1998) and shelf *Conus* and *Pteria* shells

(Fig. 12 A, C). The low $\delta^{18}O$ values exhibited by *S. alatus* imply a habitat of low salinity, low-$\delta^{18}O$ waters for most of the shell growth. This is consistent with the 7 m collection depth. The upper 10 m of the water column at this locality are consistently influenced by freshwater discharge from the Mississippi and Atchafalaya rivers as well as local sources (i.e. the Sabine River). The degree of freshwater influence appears higher for shell 2712, which was collected closer to the outflow of Calcasieu Lake and the Sabine River. The Louisiana shelf *C. austini* (0519-1, 0519-2, 0520) and Texas shelf *P. colymbus* (Pc-1-4) were collected from depths greater than 15 m and yield higher $\delta^{18}O$ values less likely influenced by low salinity waters. Finally, the high $\delta^{18}O$ for *S. calcifer* reflects the absence of freshwater influence at greater depth and the lower temperatures below the seasonal thermocline.

Mollusk shells can provide accurate isotopic temperatures (i.e. paleotemperatures) as long as $\delta^{18}O_{sw}$ can be constrained (Wefer and Berger, 1991 and references therein). To calculate oxygen isotope temperatures for aragonitic shell we employ the Grossman and Ku (1986; eq. 1) temperature equation for aragonite (ar)

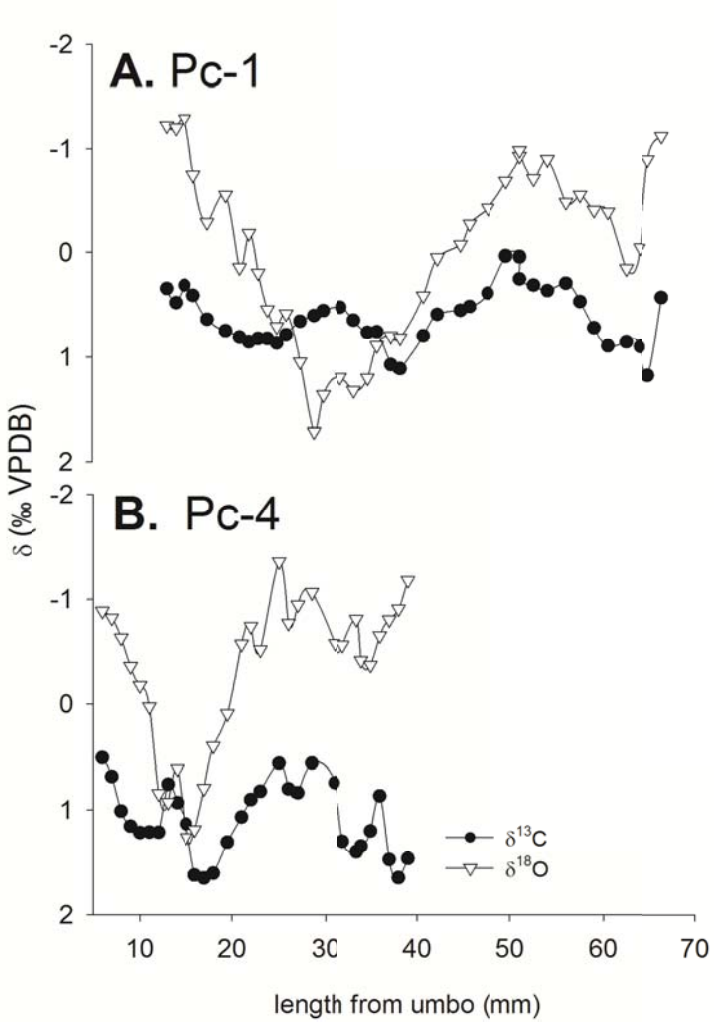

Figure 12: Isotopic profiles of *Pteria colymbus* specimens Pc-1 (A) and Pc-4 (B). Axes of δ values are reverse, as this is standard convention. The increased length of Pc-1 is because it is the larger shell valve (*Pteria* valves are not symmetric) while Pc-4 is the smaller valve.

formulated for $\delta^{18}O_{sw}$ reported versus standard mean ocean water (SMOW, and also VSMOW):

$$T°C = 19.7 - 4.34(\delta^{18}O_{ar} - \delta^{18}O_{sw}) \qquad (14)$$

Equilibrium $\delta^{18}O$ values of calcitic shells (*C. gigas* and *S. calcifer*) are lower relative to aragonite shells by about 0.8‰, and thus require a different temperature equation (Kim and O'Neil, 1997):

$$T°C = 16.1 - 4.64(\delta^{18}O_{Ca} - \delta^{18}O_{sw}) + 0.09(\delta^{18}O_{Ca} - \delta^{18}O_{sw})^2 \qquad (15)$$

Calculating isotopic temperatures from shells precipitated in marginal environments can be complicated by influence of freshwater runoff, which lowers $\delta^{18}O_{sw}$. For this study, we have used a $\delta^{18}O_{sw}$ value of 1.1‰ that is indicative of open ocean Gulf of Mexico seawater (Strauss, unpubl. data). Isotopic temperatures higher than seasonal ranges most likely indicate low seawater $\delta^{18}O$ caused by fresh water influence. Considering that salinity-$\delta^{18}O_{sw}$ trends for the LA-TX shelf show that fresh water influence is largely limited to the upper 10 m of the water column, the isotopic temperatures of *Strombus* (7 m) and *Crassostrea* (Terrebonne Bay; Kirby et al., 1998) are the only shells significantly affected by fresh water influence.

Pteria colymbus shells Pc-1 and Pc-4 yield comparable temperature ranges from 18 to 31°C. However, average values of Pc-3 and Pc-4 are 2°C cooler than Pc-1 and Pc-2 (Fig. 11). Because all four shells were found attached to the same Gorgonian, this discrepancy is likely associated with each individual's seasonal growth rate. Instrumental temperatures range from 14 to 31°C near this locality. The failure of *P.*

colymbus shells to capture the full seasonal temperature range may reflect a reduction of growth at temperatures below 18°C, or a 1‰ lowering of winter $\delta^{18}O_{SW}$ in response to water column mixing caused by frequent winter storms (Wang and Justić, 2009).

Louisiana shelf *C. austini* specimens 0519-1 and 0519-2 both yield identical temperature ranges of 20 to 29°C and averages of 24±2°C. Shell 0520 exhibits a slightly higher range of 21 to 31°C and average 26±3°C due to its shallower collection depth. These ranges agree with seasonality averages measured by NOAA Buoy 42040 (see Fig. 12). The accuracy of isotopic temperatures in *C. austini* further justifies *Conus* shells as very practical paleotemperature proxies (Gentry et al., 2008; Kobashi and Grossman, 2003; Sosdian et al., 2006).

Outer Louisiana shelf *S. calcifer* yields seasonal temperature ranges of 16 to 20°C and an average of 18±1°C. Temperature measurements are sparse for the shelf break. Seasonal temperatures from the 2009 World Ocean Atlas (Antonov et al., 2010; Locarnini et al., 2010) at 80 m depth range from 19°C - 21°C. Published $\delta^{18}O_{sw}$ values (Zerai, 2001) for outer shelf bottom waters show summer $\delta^{18}O_{sw}$ values of 1.2‰ and winter values of 0.5‰. Such a shift would increase isotopic temperatures by 2.3°C and account for the increased isotopic temperature range.

Carbon isotopes

The $\delta^{13}C$ values of shelf mollusks show higher variability than $\delta^{18}O$ values. Similar to shell $\delta^{18}O$ values, the $\delta^{13}C$ values of nearshore *S. alatus* are also significantly lower than those of shelf specimens due to fresh water influence and as with $\delta^{18}O$ values,

$\delta^{13}C$ values show that specimen 2712 is from lower salinity waters than nearby 2578 (Fig. 11).

Consistently lower $\delta^{13}C$ values are observed for shells collected since 2000 (*P. colymbus* from this study and *C. ermineus* from Gentry et al., 2008) versus shells collected during the early 1970s (*C. austini* from this study and *C. ermineus* from Kobashi and Grossman, 2003). Gentry et al. (2008) concluded that the lower $\delta^{13}C$ values of *C. ermineus* shells collected in 2003 from Stetson Bank in the Gulf of Mexico, relative to those collected in 1971 (Kobashi et al., 2003), were due to the lowering of seawater $\delta^{13}C_{DIC}$ by the invasion of ^{13}C-depleted anthropogenic CO_2 (i.e. the marine ^{13}C Suess effect). This flux has lowered the global mean surface ocean $\delta^{13}C_{DIC}$ by 0.02‰ per year from the 1970s to 1990s (Böhm et al. 1996; Gruber and Keeling, 2001; Quay et al., 1992). Comparison of the 1971 and 2003 *C. ermineus* specimens indicate a rate of anthropogenic $\delta^{13}C_{DIC}$ decrease of 0.03‰ y^{-1} (Gentry et al., 2008). $\delta^{13}C$ values of *C. austini* shells compared with those of 2003 *C. ermineus* and 2009 *P. colymbus* shells indicate comparable decreasing rates of 0.04‰ y^{-1}. This value is calculated from disparate environments, whereas the Gentry et al. (2008) value is focused on *Conus* from one offshore locality (Stetson Bank), and therefore may be a more accurate measure of anthropogenic CO_2 flux into Gulf of Mexico waters.

Pteria colymbus and *C. austini* specimens were collected from localities where hypoxia has been previously measured (Fig. 7). However, neither shell groups yield $\delta^{13}C$ values within the hypoxia range calculated from DO-$\delta^{13}C_{DIC}$ regressions (Fig. 10). This is even true for *C. austini* specimens, which were collected in 1972 and thus lived in

shelf waters less influenced by anthropogenic CO_2. Even when adjusted for a maximum ^{13}C Suess effect offset of -1.5‰, values still do not indicate hypoxia. Stable isotope profiles (i.e. isotopic growth histories of individual shells) can offer more refined information on interpretation of shelf bottom water conditions.

Stable isotope profiles

Isotopic profiles of *P. colymbus* (Pc-1, Pc-4) and *C. austini* specimens are illustrated in Figures 12 and 13. Profiles are not shown for *Strombus* shells due to obscuration by fresh water influence. Furthermore, due to the limited temperature variation at the 80-m collection site of the *S. calcifer* specimen, no distinct seasonal isotopic record is apparent.

Oxygen isotopic profiles of Pc-1 and Pc-4 exhibit growth spans slightly longer than one year (Fig. 12). Both profiles show $\delta^{13}C$ and $\delta^{18}O$ to be in phase, with each shell beginning with low values followed by a positive excursion that is then followed by a negative excursion. Additionally, both profiles end with sudden near 1‰ decreases of $\delta^{18}O$. Tracking the $\delta^{18}O$ backward from the collection date of November 6th, 2009 suggests Pc-1 and Pc-4 began depositing shell in the late summer of 2008. The discrepancy in profile length between Pc-1 (68 mm) and Pc-4 (39 mm) is the result of using different valves for each shell. As with other pearl oysters, the left and right valves of *P. colymbus* are different size (so that one locks into the other); barnacles attached to the larger valve of Pc-4 made it unsuitable for sampling. Additionally, Pc-2 and Pc-3 do not yield systematic profiles due to sampling problems brought on by encrusting organisms.

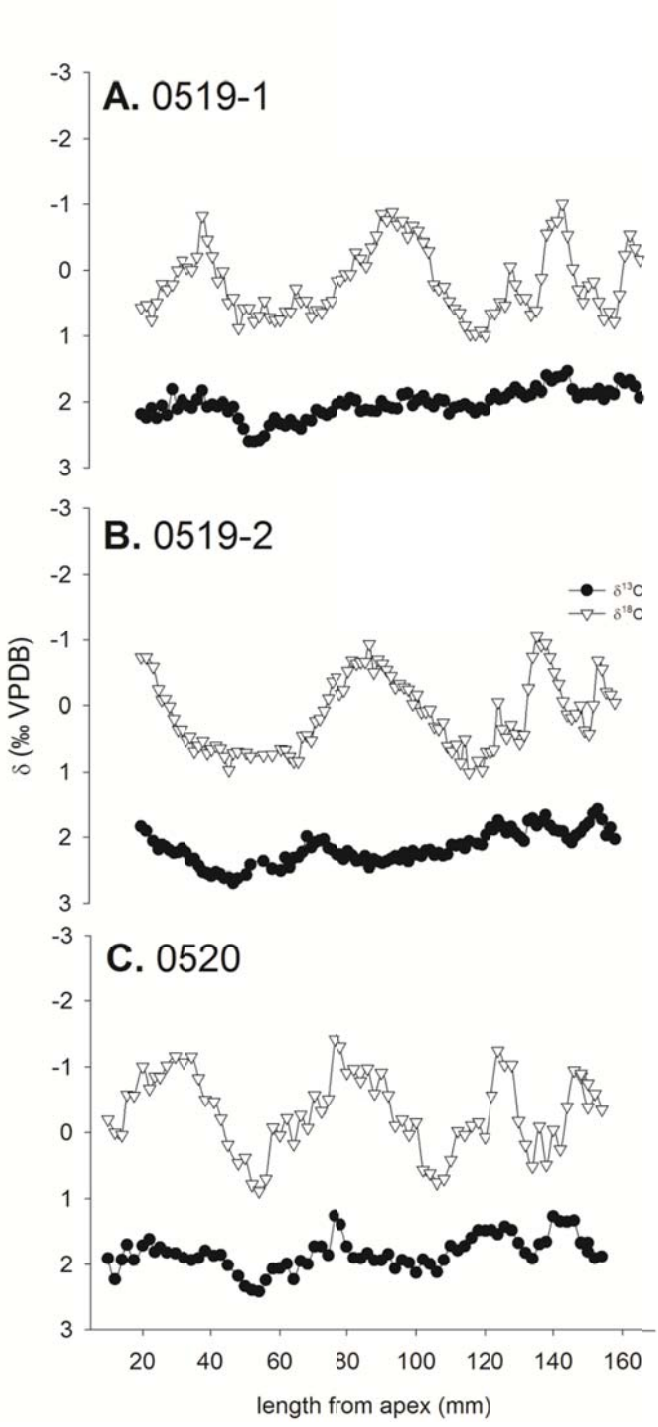

Figure 13: Isotopic profiles of *Conus austini* specimens 0519-1 (A) 0519-2 (B) and 0520 (C).

The isotopic profiles of Louisiana shelf *C. austini* specimens (0519-1, 0519-2, 0520) exhibit clear records of seasonality, with each shell spanning approximately 3 to 4 calendar years from 1968 to 1972 (all three shells were collected live on Feb. 6th of 1972) (Fig. 13). The $\delta^{18}O$ profiles of 0519-1 and 0519-2 are strikingly similar, with the same ranges and large scale features. The profile of shell 0520 is comparable to both 0519 shells, but exhibits higher intraseasonal $\delta^{18}O$ variability. This increased variability may be reflecting a more dynamic environment. As the collection depth for 0520 is shallower by 6 m compared with the 0519 shells, there may be increased, albeit limited, influence of fresh water. In all of the *C. austini* profiles, $\delta^{13}C$ values exhibit less variability than $\delta^{18}O$, and are consistently near 2‰.

Chronologic calibration of profiles

For this study we have assigned shell chronologies by calibrating shell $\delta^{18}O$ extrema to the days, with the warmest and coolest average temperatures (see *Profile Tuning* in Gentry et al., 2008). On average, the warmest day of the year for Louisiana shelf waters from 1995-2008 was August 8th, and the coldest was March 4th (reported by NOAA buoy 42040). NOAA buoy 42043 on the Texas shelf measured August 23rd as the warmest day and January 31st as the coolest. Chronologically-tuned isotopic profiles of *P. colymbus* and *C. austini* shells are illustrated in Figures 14 and 15.

Following the development of shell chronologies, growth rates can be easily calculated. Shell growth rates (Fig. 16; Table 4) of *Conus* and *Pteria* shells exhibit opposite trends. *C. austini* growth slows between the 3rd and 4th year of growth, whereas *P. colymbus* growth rate doubles from summer of 2009 to the

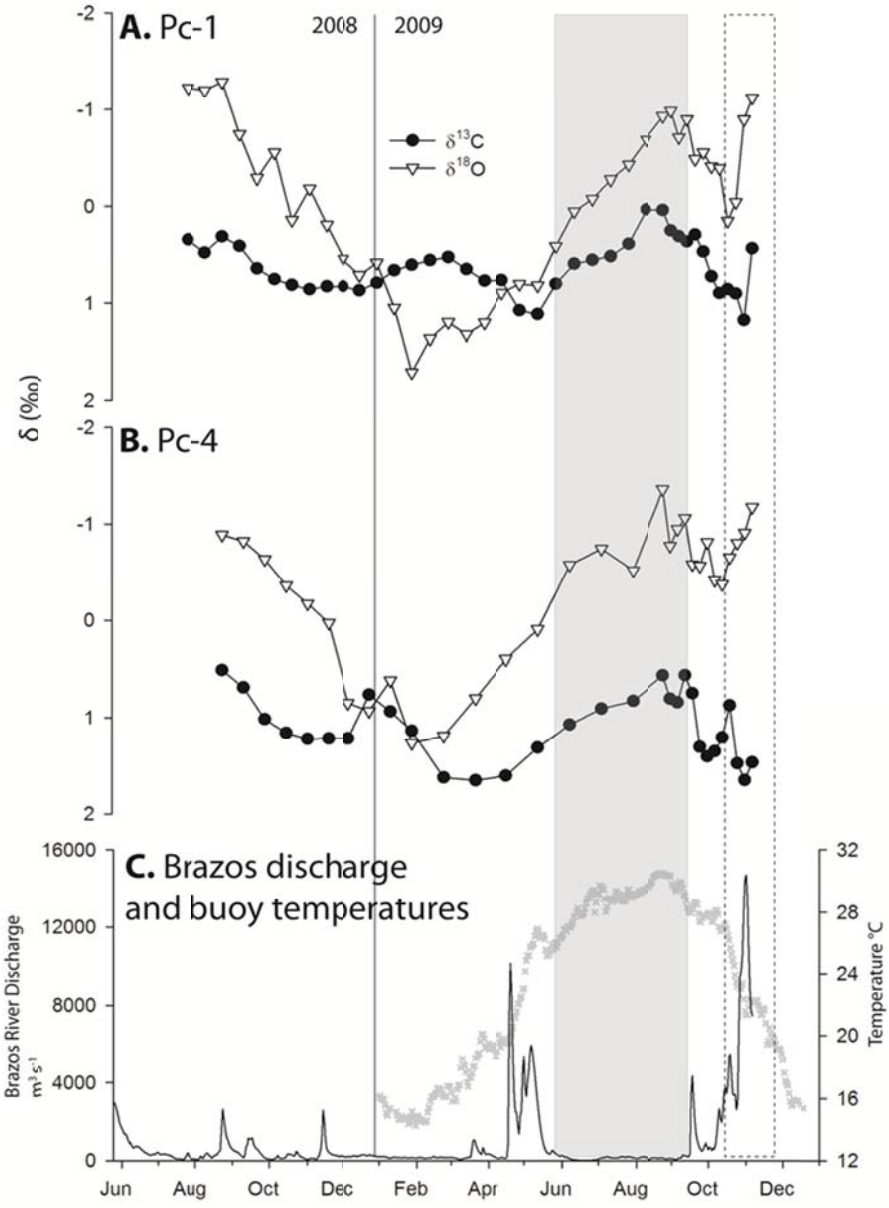

Figure 14: Chronologically-tuned isotopic profiles of *Pteria colymbus* specimens Pc-1 and Pc-4. Bottom plot shows contemporary discharge of the Brazos River and average daily temperatures measured by NOAA instrumentation buoy 42043.

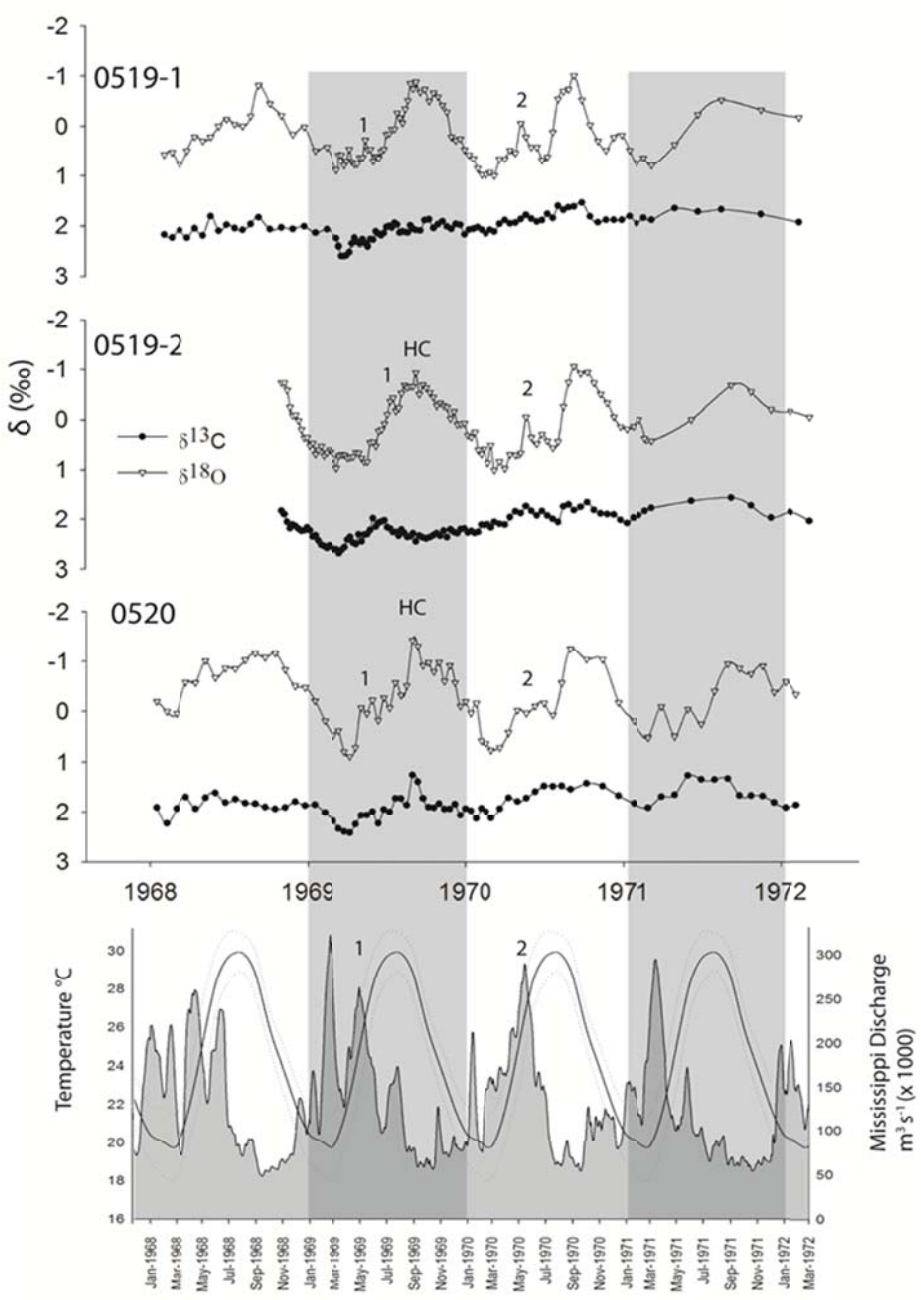

Figure 15: Chronologically-tuned isotopic profiles of *C. austini* shells 0519-1, 0519-2 and 0520. Bottom plot shows contemporary discharge of the Mississippi River and seasonal water temperatures, averaged from 1995-2008, measured at NOAA instrumentation buoy 42040 (dotted lines show 95% confidence intervals).

November, 2009 collection date. Table 4 summarizes extension rates and the length of time represented by each drilled sample (time averaging) for *C. austini* and *P. colymbus* shells.

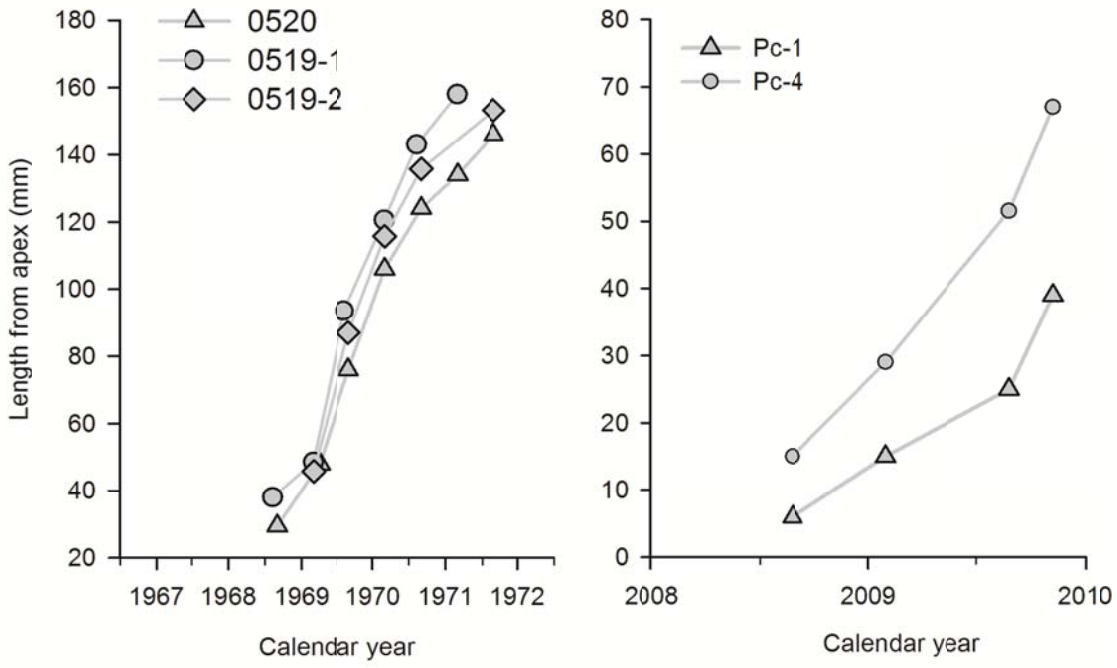

Figure 16: Shell extension rates for specimens of *C. austini* (left plot) and *P. colymbus* (right plot). The age of shell carbonate is estimated by assigning the highest and lowest shell $\delta^{18}O$ values to the coolest and warmest days within each seasonal cycle. *Conus austini* exhibit the most rapid growth during their second and third years with a decrease in shell extension beyond that point. *Pteria colymbus* exhibit more rapid growth following the first year.

Table 4: Estimated shell extension rates and days averaged within each milled sample.

Sample number	Species	Extension Rate (mm d^{-1})	Time averaging of sample (days)
0519-1	*Conus austini*	0.06 - 0.15	5 - 14
0519-2	*Conus austini*	0.05 - 0.23	4 - 16
0520	*Conus austini*	0.05 - 0.18	4 - 16
Pc-1	*Pteria colymbus*	0.09 - 0.20	4 - 9
Pc-4	*Pteria colymbus*	0.05 – 0.19	4 - 16

Freshwater penetration and benthic respiration

Rivers by far account for the largest influx of freshwater into the GoM, with the Mississippi and Atchafalaya Rivers delivering over 80% of that river discharge (Dinnel and Wiseman, 1986). The depth penetration of river waters is an indication of total water column mixing, and therefore an indication of the absence of stratification. The isotopic signal of a fresh water perturbation would appear as a sudden dramatic decrease in $\delta^{18}O$ accompanied by a depletion of shell $\delta^{13}C$ due to influence of ^{13}C-depleted river water DIC. Water column mixing during summers (when hypoxia is most severe) is generally restricted to periodic storms that may not significantly affect shell chemistry, either because of the short span of the event or because the mollusk retreats into its shell due to environmental stress (Hughes, 1986).

Mollusk shells sampled from stratified waters have been previously associated with reductions in shell $\delta^{13}C$ due to eutrophication and productivity in surface waters

(Purton and Brasier, 1997). On the Texas-Louisiana shelf, stratification is a seasonal density-driven process caused by a confluence of increased spring influx of mostly Mississippi-Atchafalaya discharge, early summer reversal of the coastal current, and a reduction of wind-driven mixing and storm activity during summers (DiMarco et al., 2005).

Comparison of *C. austini* isotope profiles with Mississippi discharge records reveals spring peak discharge events in $\delta^{18}O$ records (Fig. 15; marked as events 1 and 2 in all shells). Using the salinity-$\delta^{18}O$ relationship for Louisiana shelf waters defined in Chapter II:

$$\delta^{18}O\ (‰) = 0.17\ S - 5.0$$

the 1‰ $\delta^{18}O$ decline in shells 0519-1 and 0519-2 at event 2 represents a decrease in salinity from 36 to 31 (assuming a constant temperature of 24°C) and the 1.2‰ decline in 0520 at event 1 signifies a salinity decline to 29. The timing of peak discharge events 1 and 2 is early March, prior to development of shelf stratification. The increased Mississippi discharge prior to event 1 is not clearly recorded in any of the shells. This suggests no penetration of lower salinity waters during the spring of 1969. This may be a regular occurrence, as strongly stratified mid-April shelf waters were observed during 2008 (Bianchi et al., 2009).

A low salinity event recorded in shell 0520 occurred mid-summer of 1969 (Labeled "HC", Fig. 15), when waters are often heavily stratified. The timing of this event matches the mid-August arrival of hurricane Camille, a Category Five storm on the Saffir-Simpson scale, to the Louisiana coast, which would have thoroughly mixed

shelf waters. This event is not significantly recorded in 0519 shells. Shell 0519-2 only exhibits a $\delta^{18}O$ decrease of 0.2‰ and 0519-1 does not exhibit any $\delta^{18}O$ perturbation associated with hurricane Camille, meaning that low salinity surface waters did not penetrate to 30 m depth, or that both mollusks were not precipitating shell at that time. It is possible that they were buried in the substrate, but the rapid growth rate implies they were active and most likely feeding. Also, if submersed in pore waters, shell $\delta^{13}C$ would be influenced by ^{13}C depleted pore waters (McCorkle et al., 1985; Morse and Rowe, 1999).

The Hurricane Camille mixing event is captured by two samples of shell 0520. Based on the shell growth rate of 0.16 mm d^{-1}, a 0.8 mm width sample averages five days of growth. Two samples plus a 1 mm gap between samples (~6 days) represents roughly 16 days. Thus, for at least 16 days following the passage of Camille, low salinity surface waters penetrated to the seafloor (i.e. water column mixing). Rabalais et al. (2009) measured bottom water DO on the Louisiana shelf during the 2003 hurricane season and found Hurricane Claudette alleviated hypoxia for three days. Claudette, a r Category 1 storm, was notably weaker than Hurricane Camille .Hurricane Katrina, a storm more comparable in strength to Hurricane Camille, led to mixing of shelf waters during August, 2005; unfortunately the extent of its influence has not been measured. The $\delta^{13}C$ values of specimen 0520 show a $\delta^{13}C$ minimum corresponding to the $\delta^{18}O$ minimum, also interpreted as tracing downward mixing of Mississippi-Atchafalaya influenced surface waters during Hurricane Camille. Following the event, $\delta^{13}C$ returns to average values, if the lowered shell $\delta^{13}C$ was caused by freshwater penetration, then

these data imply that there was no storm induced respiration caused by the liberation of organic carbon from sediments (Bales, 2003; Tomasko et al., 2006).

The limited timespan of water column mixing following Hurricane Camille implies that the Louisiana shelf mollusks only experience short-term event-driven periods of fresh water influence. Under this assumption, isotope profiles of *C. austini* are predominantly tracking benthic water conditions and thus $\delta^{13}C$ values would reflect the lowering of $\delta^{13}C_{DIC}$ from respiration of organic matter. Vital effects are inconsequential considering low salinity mixing events can be extrapolated from both $\delta^{18}O$ and $\delta^{13}C$. Additionally, of the selected study sites, only upwelling on the Texas shelf may lead to depletion of $\delta^{13}C$ values not associated with benthic respiration and hypoxia, due to more ^{13}C-depleted outer shelf bottom waters.

Both 0519 shells do not exhibit significant $\delta^{13}C$ reductions during summer months. During the summer of 1970, shells 0519-1 and 0519-2 exhibit very small but similar decreases of 0.2 to 0.3‰. Both shells were collected in 30 m depth near the Mississippi Canyon drop off, a locality not hypoxic during 2008 and 2009 (Fig. 7) but included in the hypoxic region defined by Rabalais et al. (1999). Shell 0520 records gradual reductions of up to 0.6‰ from spring to summer of 1970 and 1971, with the 1971 values increasing mid-summer. At the most, a 0.6‰ reduction of $\delta^{13}C$ implies a $\approx$ 1 mL L^{-1} decrease of DO (according to equation 13). If initial DO of shelf bottom waters are assumed to range from 3-4 mL L^{-1} (Zerai 2001; Chapter II), then it is highly improbable that these shells experienced hypoxia in their 3-4 year lifespans. Although observations strongly suggest that the extent and severity of hypoxia increased during

the 20th century due to development of petroleum based fertilizers (Osterman et al., 2008), our data imply that increased respiration (and hypoxia) did not occur at these localities during 1969 and 1970.

Coastal water observations during the summer of 2009 show no hypoxia occurring over the *P. colymbus* collection locality (Fig. 7), but do indicate DO concentrations ranging from 2 to 3 ml L^{-1} (NOAA SEAMAP, 2010). Due to the young age of these specimens, 2009 was the only full year represented by the isotopic profiles. Nevertheless, the in-phase relationship between $\delta^{18}O$ and $\delta^{13}C$ observed for summer record of Texas shelf *P. colymbus* shells may indicate increased benthic respiration. According to equation 12, the maximum lowering of $\delta^{13}C_{DIC}$ from June to August of 0.6‰ (Pc-4, Fig. 14) equates to a lowering of DO by about 0.7 mL L^{-1}. Alternatively, the in-phase relationship of $\delta^{18}O$ and $\delta^{13}C$ may also be tracking decreased $\delta^{18}O_{sw}$ and $\delta^{13}C_{DIC}$ caused by fresh water mixing.

Conclusions

Oxygen and carbon isotopes of Texas- Louisiana shelf mollusk shells, when not severely influenced by low salinity waters, appear to accurately record seasonal temperatures and track shifts of the $\delta^{13}C_{DIC}$ of DIC associated with water column mixing and benthic respiration.

Stable isotope analyses of nearshore Louisiana shelf *Strombus* shells indicate mixing of the water column at 7 m depth. Isotope profiles of historically collected *C. austini* span between three and four years. The isotopic records show only storm induced

surface water penetration to the seafloor during summers. *Conus austini* $\delta^{13}C$ records exhibit a subdued respiration signal translating to a minimal decrease in DO, indicating no hypoxia at their localities from 1969-1970. *Conus austini* also suggest that the water column mixing caused by hurricane Camille significantly lowered salinity at 24 m depth but had little influence at 30 m, and that the water column restratified roughly 14 days following the storm. Texas shelf specimens of the bivalve *P. colymbus* yield isotopic records only spanning about one year. However, their isotopic profiles appear to track respiration and reduced DO concentrations in bottom waters during the summer of 2009.

Additionally, comparison of *C. austini* and *P. colymbus* $\delta^{13}C$ values with published $\delta^{13}C$ values of *C. ermineus* shells from Stetson Bank reveal a decrease in shelf water $\delta^{13}C_{DIC}$ associated with the intrusion of ^{13}C-depleted fossil fuel CO_2. The $\delta^{13}C_{DIC}$ depletion rates calculated from shells in this study are nearly double global averages and are 30% higher than previously reported rates for Gulf of Mexico waters.

CHAPTER IV

100 YEARS OF BENTHIC FORAMINIFERAL HISTORY ON THE INNER TEXAS SHELF: FAUNAL INDICATIONS AND STABLE ISOTOPES

Overview

Coastal regions, such as the Texas-Louisiana shelf, are subject to seasonal hypoxia that strongly depends on the magnitude of fresh water discharge from local and regional river systems. We have examined benthic foraminiferal fauna and isotopic compositions in two ^{210}Pb-dated box cores (BR4 and BR5) to examine the evidence for nearshore hypoxia and freshwater discharge on the Texas shelf during the last 100 years. ^{210}Pb chronologies of both cores reveal sedimentation rates of 0.2 and 0.1 cm y^{-1}, translating to ~60 and ~90 year records. The fauna of both cores were almost exclusively composed of *Ammonia parkinsoniana* and *Elphidium excavatum*, indicating euryhaline ambient waters. The *Ammonia-Elphidium* (A-E) index, a qualitative measure of low oxygen conditions, of both cores shows an increase from values between 20 and 50 to near 100, indicating low oxygen conditions between 1960 and the core top. Between 1950 and 1960 (9-10 cm), low A-E values in BR4 coincide with high δ^{18}O and δ^{13}C values greater than 0‰ and -1‰ respectively. These values correspond to a period of severe drought (the Little Dust Bowl) over the Brazos River drainage basin and considerably reduced river discharge from 1948-1957. The event is also marked by increased specimen weights for *E. excavatum*. High A-E values prior to this event imply low-oxygen conditions were prevalent prior to anthropogenic exacerbation of Louisiana

shelf hypoxia and at least since the dredging of a new Brazos River delta in 1929. *Elphidium excavatum* $\delta^{13}C$ values are very low (-4‰) and indicative of a previously documented *vital effect.* $\delta^{13}C$ values of *A. parkinsonia* average -3‰ and exhibit little variability, most likely reflecting pore waters influenced by aerobic and anaerobic respiration. The association of lowered Brazos River discharge with more oxygenated shelf bottom waters suggests Brazos River discharge and shelf hypoxia are linked, however influence of Mississippi-Atchafalaya discharge can also contribute to shelf stratification.

Introduction

The exacerbation of eutrophication-driven hypoxia (where dissolved oxygen falls below 1.4 ml L^{-1}) in the last century, due to increased fertilizer use and modification of the Mississippi River delta, has created a recurring summer dead zone on the Louisiana and Texas shelf (Rabalais et al., 2002b; Bianchi et al., 2009; 2010). Hypoxia in the northern Gulf of Mexico commonly occurs west of the Mississippi River delta, often in depths of 30 m or less, and occasionally extends onto the Texas shelf (Fig. 17) (Harper et al., 1981; Rabalais et al., 2001). Hypoxia on the Texas shelf is often associated with westward migration of Mississippi-Atchafalaya discharge, but can also be instigated by events of increased local runoff. For example, in 2007, late spring flooding of the Brazos River induced middle Texas shelf hypoxia, whereas 2008 hypoxia in the same region was traced to above average Mississippi-Atchafalaya discharge (DiMarco et al., submitted). Texas shelf hypoxia surveys have only recently become routine via the

NOAA SEAMAP program. Moreover, prior observations do not indicate whether hypoxia on the Texas shelf existed before the anthropogenic intensification of Louisiana shelf hypoxia and whether Brazos River discharge is regularly responsible for its formation.

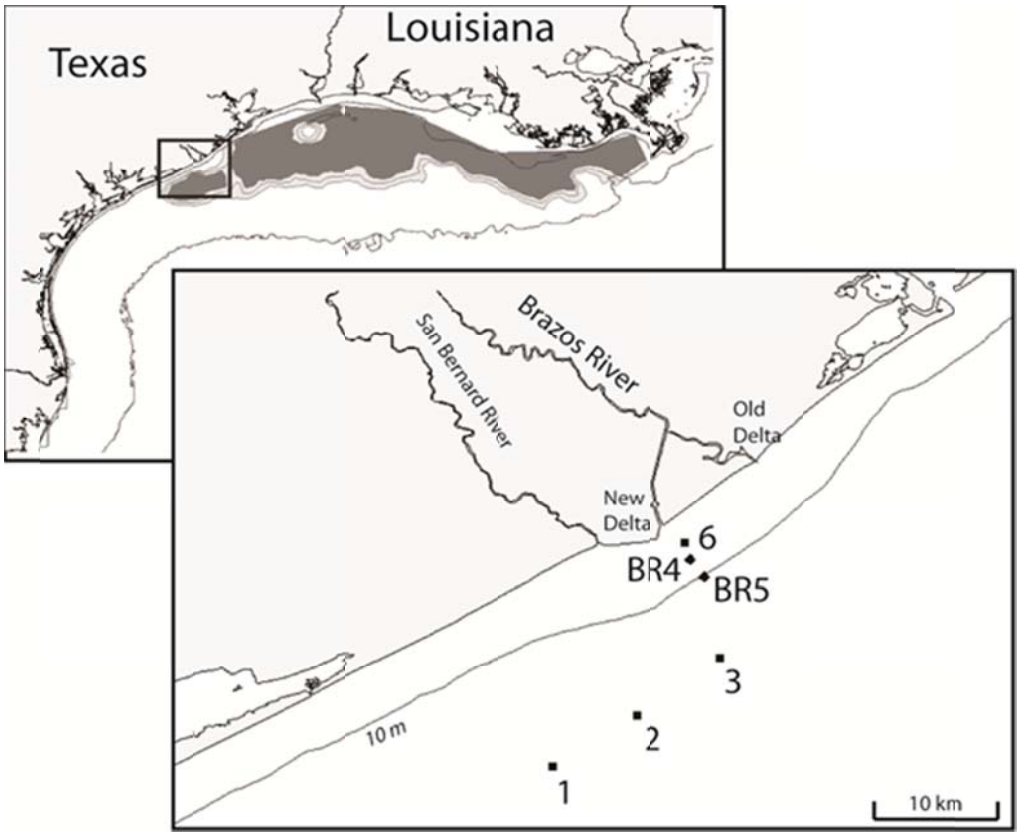

Figure 17: Background: Map of Texas-Louisiana shelf highlighting the size of the 2008 hypoxic zone. Hypoxic waters (DO < 2 mg L^{-1}) are shaded dark grey while low oxygen waters (DO < 3 mg L^{-1}) are shaded light grey. Foreground: 2008 box core (BR4, BR5) and water sampling stations (all locations). The transition to the new Brazos River delta took place in 1929.

In addition to potentially creating hypoxic conditions, discharge from the Brazos River and nearby rivers regulates estuarine salinities. Reduced discharge events, often associated with droughts, can threaten oyster and mollusk populations (Norwine et al., 2007) as well as recreational and commercial fish stocks (Harvey, 2009). Furthermore, under global warming scenarios, these drought events will likely become more recurrent and severe (North et al., 1995).

Benthic foraminifera from coastal sediments may yield insight into the periodicity and severity of drought and shelf hypoxia. Foraminifera from box and piston cores have been used to assemble historic records of hypoxia on the Louisiana shelf (Sen Gupta et al., 1996; Osterman et al., 2008; 2009). Some foraminiferal genera are better adapted to low oxygen conditions and provide indications of hypoxia. Osterman (2003) measured abundances of benthic foraminifers from core-top sediment samples and found that *Pseudononion atlanticum*, *Epistominella vitrea*, and *Buliminella morgani* (PEB) were associated with low oxygen, hypoxic waters. Osterman defined the PEB index as the percentage of these three genera relative to the total benthic foraminiferal abundance, and revealed that southern Texas shelf waters may be susceptible to recurring hypoxia (Osterman, 2003).

To determine the relative importance of Brazos River discharge on Texas shelf hypoxia and examine the periodicity of drought events, we have investigated the faunal abundance and stable isotopes of foraminifera collected on the Texas coast near the Brazos River delta. The predominance of estuarine versus more marine foraminifera facies can yield qualitative interpretation of shelf salinity, which is linked to both

hypoxic and drought events. Oxygen and carbon stable isotopes ($^{13}C/^{12}C$, $^{18}O/^{16}O$, hereon $\delta^{13}C$ and $\delta^{18}O$) of benthic foraminifera are widely-used paleoceanographic proxies for Earth history (Zachos et al., 2001). Foraminifera $\delta^{18}O$ have been used as tracers of temperature, salinity and water masses (Waelbroeck et al., 2002; Eberwein and Mackensen, 2008), and thus may provide historical measurements of Brazos River influence in shelf waters. Additionally, foraminiferal $\delta^{13}C$ have been used as indicators of bottom and pore water respiration (McCorkle et al., 1997), so that these measurements could yield insight into bottom water oxygen levels. We have also supplemented previous salinity and $\delta^{18}O$ records of shelf water (DiMarco et al., submitted) with contemporaneous measurements of DO and $\delta^{13}C$ of the dissolved inorganic carbon ($\delta^{13}C_{DIC}$).

Methods

Two 7.6 cm inner diameter subcores were collected from 0.5 m box cores retrieved on the middle Texas shelf from Brazos River prodelta sediments on May 25th, 2008. Box core BR4 recovered 23 cm of sediment from 12 m water depth at 28.83°N, 95.34°W; box core BR5 recovered 13 cm of sediment from 10 m water depth at 28.85°N, 95.35°W. Several other box cores were recovered at stations further offshore (where additional water observations were made) (Fig. 17), but sediments were sandy and did not contain foraminifera. At all stations, surface and bottom seawaters were analyzed for DO in the field using a YSI multiprobe device. Water samples were collected for analysis of salinity, $\delta^{18}O$ and $\delta^{13}C_{DIC}$ using a bucket and a Niskin bottle.

$\delta^{13}C_{DIC}$ samples were stored in pre-evacuated 25 mL serum bottles pre-poisoned with $HgCl_2$ and capped with 20 mm thick septum stoppers (Bellco™ 2048-11800) sealed with aluminum crimps. Once collected, $\delta^{13}C_{DIC}$ samples were stored on ice in the field and kept refrigerated in the laboratory. Due to the reactive nature of $\delta^{13}C_{DIC}$ samples, analyses were performed within 45 days of collection. Sub-cores were refrigerated after collection, then extruded and sectioned in 1 cm increments. Core samples were then refrigerated. To sample for foraminifera, 30 mg sediment aliquots were washed in a sodium hexametaphosphate solution to dissagregrate grains, and then were sieved using a 100 mesh (149 μm) sieve. The coarse fraction was dried overnight at 70°C. Foraminifera were counted in 1 cm increments for BR5 and 3 cm increments for BR4. Foraminifera were sampled for stable isotopes in 1 cm increments in BR5 and at select increments in BR4.

Analytical methods

^{210}Pb activities were measured indirectly using the ^{210}Po method (Nittrouer et al., 1979; Santschi et al., 2001). Sediments were wet sieved with a minimum amount of deionized water through a 40 μm sieve and the smaller fraction was used to minimize the influence of changes in surface area on activity. One gram aliquots of dried sediment were spiked with a ^{209}Po tracer for yield determination. Then aliquots were prepared by complete digestion with HCl, HNO_3 and HF. ^{210}Po and ^{209}Po were chemically separated and spontaneously deposited onto Ag planchetts (Santschi et al., 2001). Activity of the Po isotopes was determined by α-spectroscopy using a Canberra surface barrier detector. ^{210}Po is the granddaughter of ^{210}Pb and is assumed to be in

secular equilibrium. ^{210}Pb activity was calculated and supported values were subtracted to determine excess $^{210}Pb_{xs}$ activity ($^{210}Pb_{xs}$). Supported values were determined by assuming that the activity at the bottom of the core where $^{210}Pb_{total}$ becomes constant is the supported value. ^{210}Pb chronologies were determined using different sub-cores than those used to collect foraminifera.

Sediment accumulation rates were determined by calculating a regression line in an area of the core consistent with steady-state deposition and using the equation:

$$S = \frac{z\lambda}{\ln\frac{A_d}{A_o}} \quad (16)$$

where S = sediment accumulation rate, z = change in depth of the regression (cm), A_d = $^{210}Pb_{xs}$ activity at end of the regression (dpm g^{-1}), A_o = $^{210}Pb_{xs}$ activity at beginning of regression (dpm g^{-1}), and λ = radioisotope decay constant (^{210}Pb, 0.031 y^{-1}) (Nittrouer et al., 1979; Santschi et al., 2001).

Salinity was measured in bottom and surface waters using a Guildline Autosal salinometer at the Geochemical and Environmental Research Group. Water samples were analyzed for $\delta^{18}O$ at Texas A&M University's Stable Isotope Geosciences Facility (SIGF). The $\delta^{18}O$ analyses were carried out using an equilibration method, where 250 µL aliquots of water were injected into septa-capped vials filled with 99.7% He and 0.3% CO_2. Waters were equilibrated for two days at a constant temperature of 22°C. Water samples were analyzed for $\delta^{13}C_{DIC}$ by acidifying 500 µL aliquots of seawater with 50 µL of phosphoric acid in an airtight exetainer vial flushed with ultra-high purity He at room temperature (Torres et al., 2005). Headspace CO_2 of $\delta^{13}C_{DIC}$ prepared vials were analyzed using a Thermo Finnigan DeltaPlusXP Isotope Ratio Mass Spectrometer

attached to a GasBench II automated gas preparation and delivery system. $\delta^{13}C_{DIC}$ values were calibrated against the NBS-19 carbonate standard ($\delta^{13}C$ = 1.95‰) and precision determined by an in-house $NaHCO_3$ solution was 0.1‰ or better.

Foraminifera were washed with Milli-Q grade water and then gently sonicated (30% power using a voltage regulator) in methanol and dried at 70°C. One to six mono-specific foraminifera, weighing from 12 to 30 µg, were digested in nearly pure H_3PO_4 (specific gravity = 1.93) at 70°C on a Thermo Finnigan Kiel IV automated carbonate device. The evolved CO_2 was then analyzed on a Thermo Finnigan MAT 253 isotope ratio mass spectrometer at the SIGF in the College of Geosciences, TAMU. $\delta^{13}C$ and $\delta^{18}O$ values were calibrated against the NBS-19 carbonate standard ($\delta^{13}C$ = 1.95‰, $\delta^{18}O$= -2.20‰) with precisions of 0.1‰ and 0.06‰ respectively, with lowered precision associated with low-weight samples. Mono-specific aliquots were analyzed to avoid mixing species-specific vital and microhabitat effects. If multiple foraminifera were used in a single analysis, care was taken to ensure specimens were of similar size. Thus, sample weights provide a measure of average foraminifera weight of analyzed specimens.

Results

Seawater salinity, DO and stable isotope compositions for May, 2008 indicate a mixed water column. Surface water salinity averaged 29.3±0.5, slightly lower than the bottom water average of 30.7±0.5. Surface salinity decreases with proximity to the delta, but only by about 0.5. No hypoxia was detected during sampling. DO concentrations of

bottom and surface waters were near saturation, ranging from 4 to 5 ml L^{-1}. Sea conditions (~2 m swell) during the sampling cruise suggested water column mixing. As with salinity, average surface $\delta^{18}O$ was slightly lower (-0.2‰) than bottom waters values (0‰). $\delta^{13}C_{DIC}$ of bottom and surface waters both averaged -0.4‰ (Table 5).

BR4 and BR5 sediments are predominantly siliceous silts and clays interbedded with thin sandy layers. ^{210}Pb chronologies show sedimentation rates are significantly different at both sites: site BR 4 exhibited a rate of 0.10 cm y^{-1} and BR5 yielded a faster rate of 0.19 cm y^{-1}. X-radiographs of box-core sediments reveal well developed laminations and no indication of bioturbation. ^{210}Pb derived sedimentation rates are only accurate for the upper 12 cm of BR 4 and upper 10 cm of BR5; and ^{210}Pb results show non-linear sedimentation below these intervals (Fig. 18). These upper core sections correspond to maximum ages of 1942 for BR4 and 1913 for BR 5. The error associated with ^{210}Pb chronologies of BR4 ranges from ±1 in the youngest sediments to ±2 years at the chronology limit; whereas BR5 error ranges from ±2 years in the youngest sediments to ±9 years at the chronology limit. The lower error for BR4 ages is attributed to the higher sedimentation rate and more precise ^{210}Pb results.

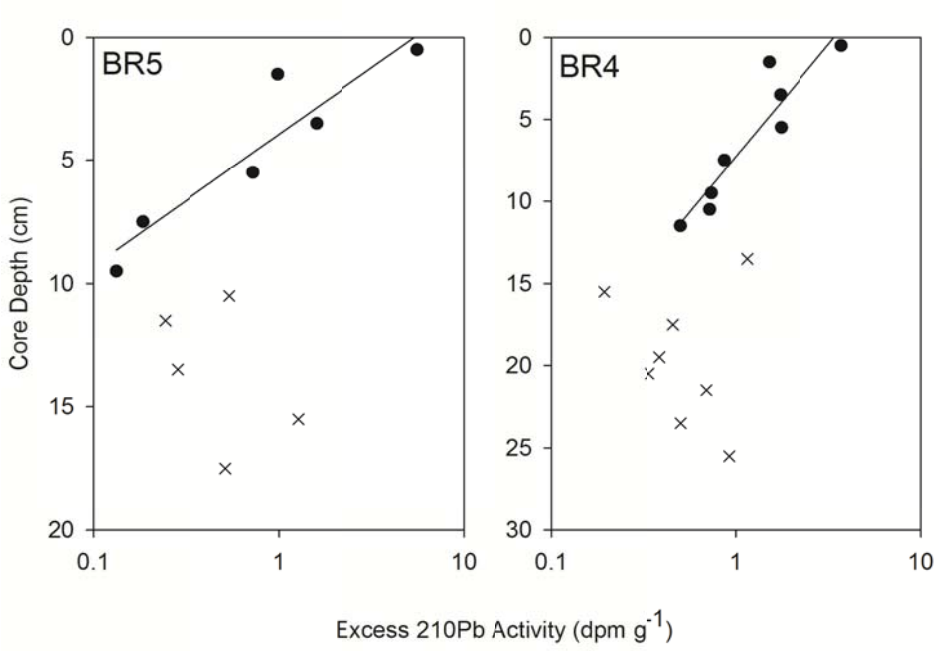

Figure 18: Excess ^{210}Pb activity measured in Texas shelf cores BR4 and BR5. Black circles indicate values used to determine sedimentation rates. X symbols mark values not used in determination of sedimentation rates.

Table 5: Water and core sampling stations and isotope, salinity, and DO measurements of shelf waters. Salinity and $\delta^{18}O$ are reported in DiMarco et al. (submitted).

STATION	Longitude	Latitude	Sample Depth (m)	Station Depth (m)	Salinity*	DO (ml L^{-1})	$\delta^{18}O$* (‰)	$\delta^{13}C_{DIC}$ (‰)
1	95.48 W	28.66 N	0	21	29.97	-	-0.3	-0.3
1	95.48 W	28.66 N	20	21	31.36	-	0.2	-0.5
2	95.40 W	28.71 N	0	18	28.70	4.6	-0.3	-0.4
2	95.40 W	28.71 N	17	18	31.11	4.0	0.1	-0.3
3	95.33 W	28.76 N	0	18	28.91	4.9	-0.2	-0.6
3	95.33 W	28.76 N	17	18	30.75	4.6	0.1	-0.4
BR4	95.34 W	28.83 N	0	12	29.30	4.6	-0.2	-0.4
BR4	95.34 W	28.83 N	11	12	30.21	5.1	0.0	-0.3
BR5	95.35 W	28.85 N	0	10	29.37	4.5	-0.2	-0.7
BR5	95.35 W	28.85 N	9	10	30.11	5.0	-0.1	0.0
6	95.36 W	28.86 N	0	8	29.54	4.8	-0.1	-0.3
6	95.36 W	28.86 N	7	8	30.51	4.0	0.0	-0.8

Table 6: Ranges and averages of foraminifera stable isotope compositions for each core.

Core/Species	Average $\delta^{18}O$ (‰)	Minimum $\delta^{18}O$ (‰)	Maximum $\delta^{18}O$ (‰)	Average $\delta^{13}C$ (‰)	Minimum $\delta^{13}C$ (‰)	Maximum $\delta^{13}C$ (‰)
BR4						
A. parkinsoniana	-1.2±0.6	-2.5	-0.1	-2.7±0.6	-3.8	-0.4
E. excavatum	-0.8±0.6	-2.0	0.6	-2.9±1.2	-4.4	1.3
BR5						
A. parkinsoniana	-1.9±0.5	-2.7	-1.2	-2.4±0.4	-3.2	-1.8
E. excavatum	-1.1±0.8	-2.5	1.0	-2.7±1.2	-4.2	-0.3

Total foraminiferal abundance from both cores ranged from 1 to 103 per undried 30 mg sediment aliquot. The assemblage was dominated (>95%) by two benthic foraminiferal species: *Ammonia parkinsoniana* and *Elphidium excavatum* (Fig. 19). No PEB fauna were observed in either core, although specimens of *Elphidium mexicanum, Hanzawaia concentrica* and *Quincueloculina bicostata* occurred at random intervals. The core localities were within the *Ammonia-Elphidium* zone described by Poag (1981), which extends throughout the marginal waters south of Galveston Bay and onto the Mexican shelf. Box core sites further offshore (sites 1-3, Fig. 17) yielded sandy sediments nearly free of benthic foraminifera. Weights of individual specimens of both species varied with depth in the core (Fig. 20). Average weights of *E. excavatum* ranged from 4 to 14 µg in pre-1942 core depths and from 5 to 25 µg for the 1942 to 1970 interval. The majority of *A. parkinsonia* specimens weighed within 4 to 8 µg, but large specimens periodically occurred. Four 14 to 16 µg specimens were found in sediments

ranging in age from 1968 to 1995, whereas only two large specimens were found prior. *Ammonia* are known to be infaunal. The *E. excavatum* specimens were unkeeled, also suggesting an infaunal habitat (Murray, 2006).

$\delta^{18}O$ and $\delta^{13}C$ ranges of each species are similar for both cores (Table 6). BR4 *E. excavatum* $\delta^{18}O$ values (mean = -0.8±0.6‰) are slightly higher than those for *A. parkinsoniana* (mean = -1.2±0.6‰), whereas BR5 *E. excavatum* $\delta^{18}O$ values (mean = -1.1±0.8‰) exhibit a larger difference from *A. parkinsoniana* (mean = -1.9±0.8‰). The $\delta^{13}C$ extrema of *E. excavatum* are consistently about 1‰ lower than *A. parkinsoniana*, however averages are similar. There are no correlations between $\delta^{18}O$ and $\delta^{13}C$ of either

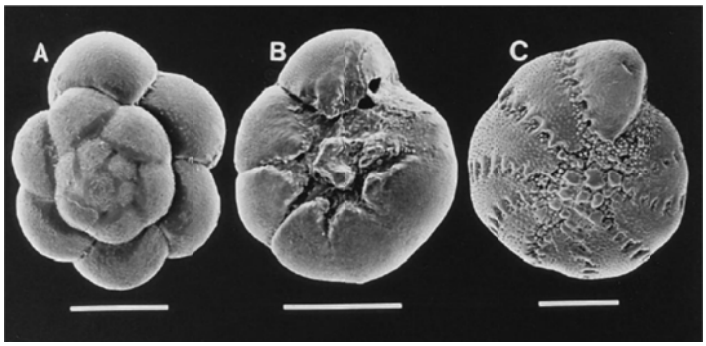

Figure 19: SEM images of *A. parkinsoniana* (A is the dorsal view and B is the ventral view) and the dorsal view of *Elphidium excavatum* (C). Scale bars represent 100 μm. From Sen Gupta et al. (1996).

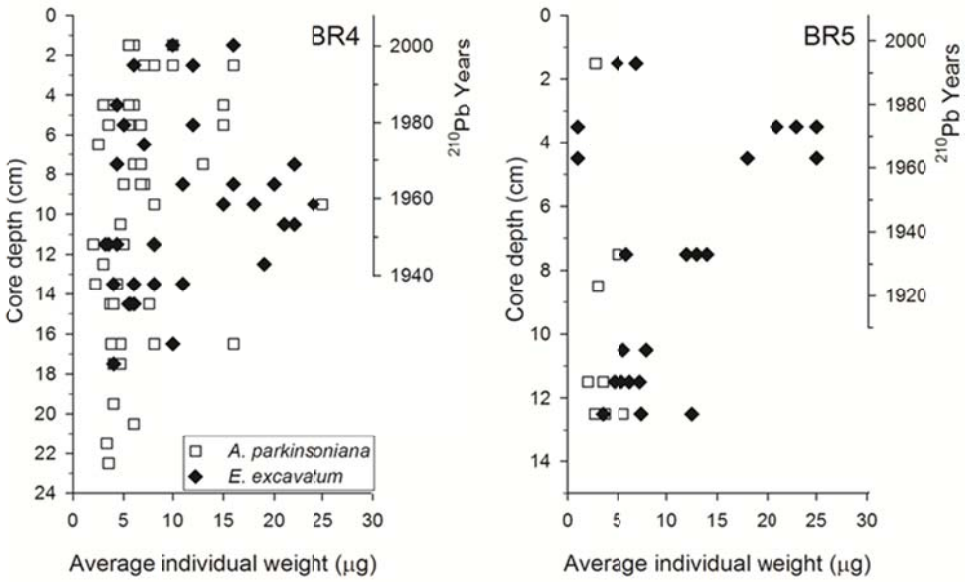

Figure 20: Average weights of individual foraminiferal tests for cores BR4 and BR5. *Ammonia parkinsoniana* generally weigh less, although some exceptions exist. *Elphidium excavatum* exhibit larger weight ranges. The weight increase of *E. excavatum* from 1950-1970 in BR4 correlates with severe drought over the Texas mainland and reduced Brazos River discharge. The similar *E. excavatum* weight increase observed in BR5 is likely related to the event, as the ^{210}Pb ages for this core were less precise.

species or between foraminifer weights and $\delta^{18}O$ or $\delta^{13}C$ (Fig. 20). *Ammonia parkinsonia* $\delta^{18}O$ and $\delta^{13}C$ do not show any large shifts or excursions with core depth in either BR4 or BR5, although the number of BR5 values are limited (Fig. 22). On the contrary, BR4 *E. excavatum* exhibit a negative $\delta^{18}O$ excursion to ~-1.1‰ at 14 cm and a positive excursion to 0.4‰ between 9 and 10 cm (1955-1960). This positive $\delta^{18}O$

excursion is accompanied by a positive shift of *E. excavatum* $\delta^{13}C$ values from between -4 and -3‰ to up to 0.6‰. BR5 *E. excavatum* $\delta^{18}O$ and $\delta^{13}C$ values show high variability between 3 and 5 cm depth, with $\delta^{18}O$ ranging from -2.5 to 0.2‰ and $\delta^{13}C$ ranging from -4.2 to -0.3‰ (Fig. 21).

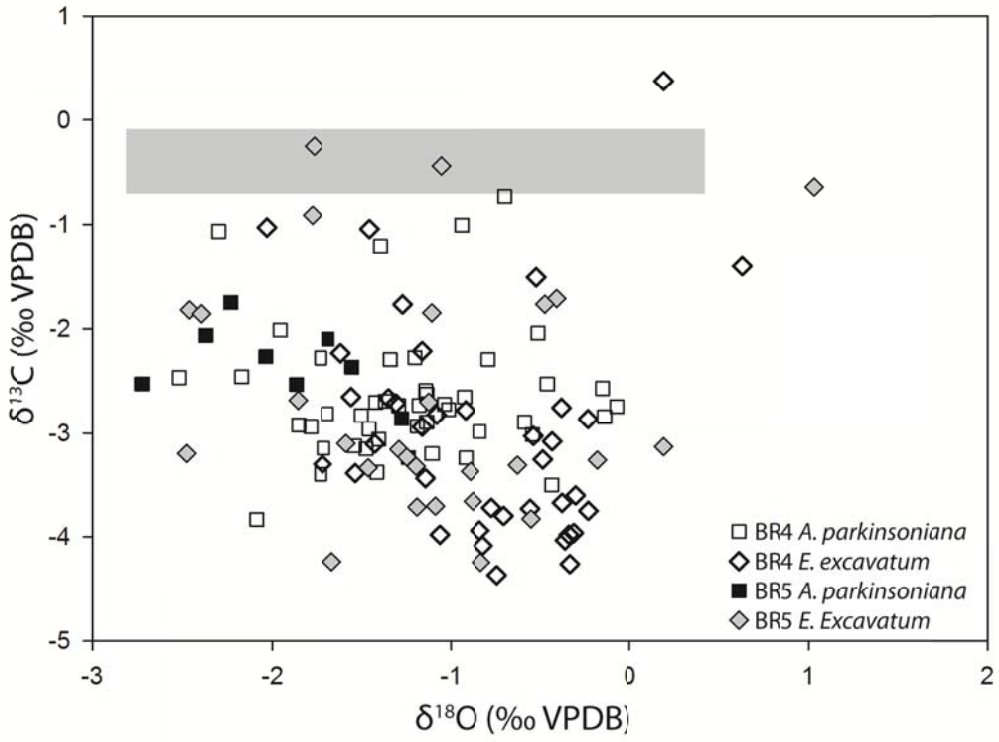

Figure 21: Scatter plot of isotope values for *A. parkinsoniana* and *E. elphidium* from cores BR4 and BR5. Note the lack of correlation between $\delta^{18}O$ and $\delta^{13}C$ for either species. The gray area represents the $\delta^{18}O$ of equilibrium calcite for the annual temperature range reported by TABS buoy 40234 (Kim and O'Neil, 1997) and the $\delta^{13}C_{DIC}$ range of bottom waters (Table 5).

Discussion

Faunal distribution and A-E index

The dominance of *A. parkinsoniana* and *E. excavatum* in coastal cores is typical. *Ammonia parkinsonia* is the most common foraminifera observed in sediments under marginal northern Gulf of Mexico waters (Poag, 1981). However, the taxonomy of *Ammonia* can be confusing (Hayward et al., 2004), with multiple phenotypes that are associated with environmental variability (i.e. ecophenotypes), particularly salinity and temperature (Holzmann, 2000). Molecular evidence suggests *Ammonia* species are geographically distributed, with only tropical to subtropical species being panoceanic (Hayward et al., 2004). *Elphidium excavatum* also exhibits considerable ecophenotypic variation with respect to temperature (Feyling-Hanssen, 1972). In general, *Elphidium excavatum,* although found in marginal environments, are less tolerant of low-oxygen conditions than *A. parkinsonia* (Sen Gupta et al., 1996).

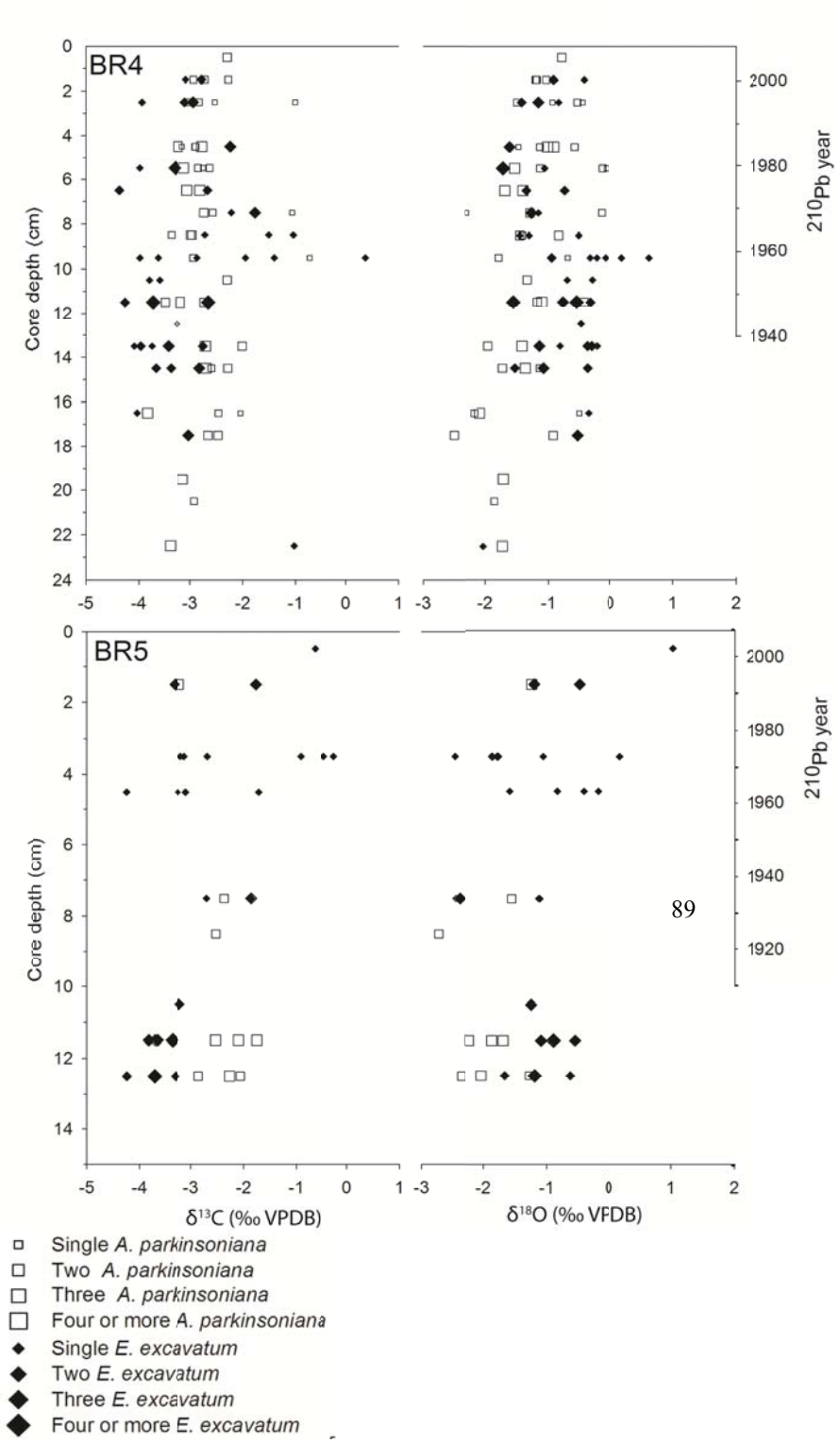

Figure 22: Stable isotope profiles of *A. parkinsoniana* and *E. excavatum* in cores BR4 and BR5. The symbol size reflects the number of foraminifera analyzed in a single isotopic measurement. Increases of BR4 *E. excavatum* $\delta^{18}O$ and $\delta^{13}C$ in the late 1950s correlate to severe Texas drought and reduced Brazos River discharge.

Thus, relative abundances of *E. excavatum* and *A. parkinsonia* can be used as qualitative indicators of low oxygen waters in coastal sediments. The *Ammonia-Elphidium* (A-E) index was defined by Sen Gupta et al. (1996) as

$$\text{A-E index value} = \frac{N_A}{N_A+N_E}\ x\ 100 \qquad (17)$$

so that periods of increased hypoxia are reflected by high A-E values.

^{210}Pb-dated cores from the Louisiana shelf show a sharp increase in A-E index during the middle-late 20th century (1940-1980) and a positive correlation between A-E index and sedimentary OC content (Sen Gupta et al., 1996). Texas shelf cores BR4 and BR5 show two periods of low A-E index values (Fig. 23). One occurs prior to 1940 and the other occurs between 1942 and 1965 in BR4 and between 1960 and 1980 in BR5. The asynchrony may arise because age calibration of BR5 is less precise than that of BR4 due to more variable ^{210}Pb results. Furthermore, lower core penetration of BR5 increases the possibility for discrepancy between sub-cores sampled for chronology and foraminifera. Considering these factors, we believe that the low A-E values between 1960 and 1980 in BR5 are contemporary with the low A-E event at 1940-1965 in BR4. Following this event, both cores exhibit an increase to high A-E values in the modern. This increasing A-E trend matches similar observations on the Louisiana shelf associated with increased hypoxia (Sen Gupta et al., 1996; Osterman et al., 2008, 2009). However, high A-E index values prior to the low A-E events imply low oxygen conditions existed

before the anthropogenic exacerbation of low oxygen conditions on the Louisiana and southern Texas shelves (Osterman, 2003; Osterman et al., 2008; 2009). Thus, BR4 and BR5 bottom waters may be normally oxygen deprived.

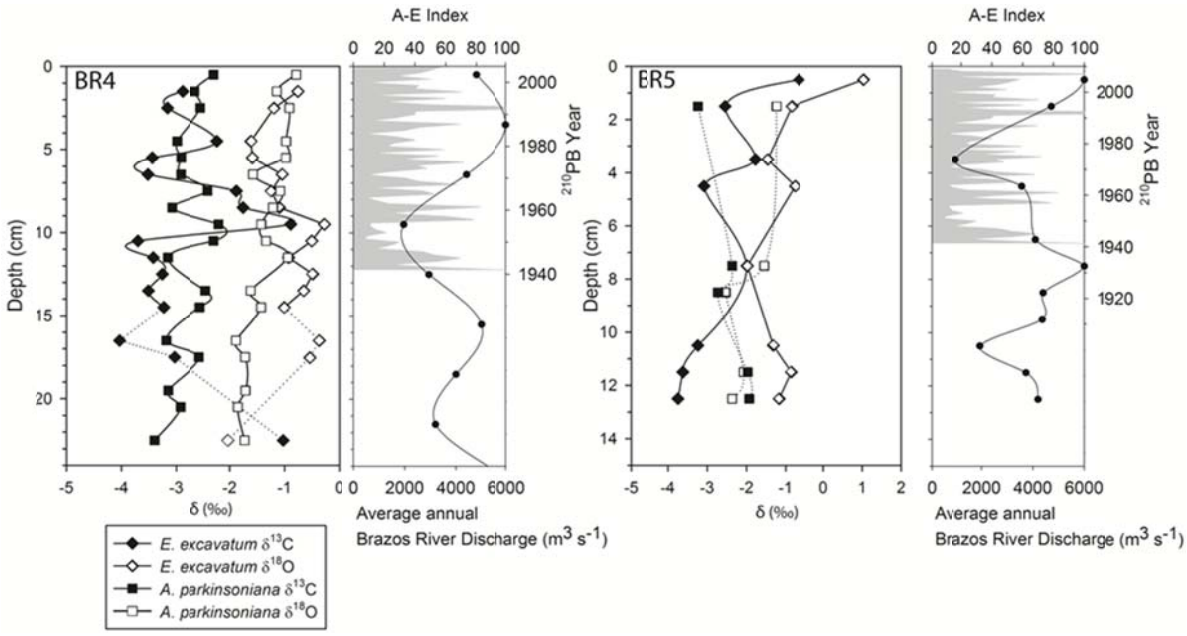

Figure 23: Average $\delta^{13}C$ and $\delta^{18}O$ of foraminifera, weighted by the number of mono-specific foraminifera per analysis, as well as A-E index values for BR4 and BR5. Dotted lines of represent trends inferred from few measurements. Annual average discharge of the Brazos River at Richmond, TX (U.S. Geological Survey, 2008), is also shown. Increased A-E values are indicative of lower oxygen conditions, while low values indicate more oxygenated bottom waters. The LDB correlates with low A-E index values while the dredging of the new Brazos River delta corresponds to increased A-E values.

The chronological offset of low A-E values in BR5 is attributed to less precise chronology of BR5.

Oxygen isotopes

The $\delta^{18}O$ of foraminiferal tests are dependent largely on three factors: temperature, the $\delta^{18}O$ of ambient water, and vital effects. Empirically-derived equilibrium relations have been developed based on measurements of natural biogenic $CaCO_3$ and synthetic $CaCO_3$ grown under known temperature and $\delta^{18}O_{sw}$ (Epstein et al., 1953; O'Neil et al., 1969; Grossman and Ku, 1986; Kim and O'Neil, 1997). If temperature ranges are limited, $\delta^{18}O$ can track salinity (Duplessy et al., 1991). Varying vital effects have been reported for *E. excavatum,* ranging from $\delta^{18}O$ enrichment relative to calcite equilibrium of 0.5 to 1.1‰ (Grossman, 1987; Thomas et al., 2000) to depletion of about 1‰ (McCorkle et al., 1997). *Ammonia* are known to exhibit minimal $\delta^{18}O$ vital effects (Chandler et al., 1996; Grossman, 1987). According to Murray (1996), the predominant temperature range for growth of *Elphidium* and *Ammonia* in the Gulf of Mexico is from 14 to 20°C and 10 to 32°C respectively. If correct, *Ammonia* likely grow year round, whereas *E. excavatum* reflect winter conditions. However, Poag (1978) has observed both species to be associated with warm Texas bay and shelf waters. Isotopic temperatures calculated using the Kim and O'Neil (1997) temperature equation,

$$T°C = 16.1 - 4.64(\delta^{18}O_C - \delta^{18}O_{sw}) + 0.09(\delta^{18}O_C - \delta^{18}O_{sw})^2 \qquad (18)$$

where $\delta^{18}O_{sw}$ = 0‰ (Table 5), show *A. parkinsoniana* to inhabit warmer waters than *E. excavatum* (Table 7). Alternatively, this may reveal ^{18}O-enrichment (i.e. vital effect) for

E. excavatum. According to temperatures provided by Texas A&M Buoy System (TABS) buoy 42035 (29.25° N, 94.41° W), the average isotopic temperatures of 20 to 21° C reported by *E. excavatum* reflect spring and late fall growth, however correction for ^{18}O-enrichment (vital effect) may lower isotopic temperatures by 2 to 5°C. The roughly 2‰ δ^{18}O ranges reported for BR4 *E. excavatum* and *A. parkinsoniana* equate to a temperature range of 10°C, suggesting specimens growing nearly year round. Under this assumption, only the δ^{18}O extrema track salinity variations induced by river discharge. Additionally, δ^{13}C extrema can also be indicative of increased river influence, as the δ^{13}C of river water is lower (< -4‰) compared with that of seawater (> 0‰).

Table 7: Ranges and averages of isotopic temperatures calculated from foraminifera δ^{18}O using Kim and O'Neil (1997).

Core/Species	Average Temp (°C)	Minimum Temp (°C)	Maximum Temp (°C)
BR4			
A. parkinsoniana	22 ±3	16	28
E. excavatum	20 ±3	13	26
BR5			
A. parkinsoniana	25 ±3	22	29
E. excavatum	21 ±4	11	28

A 0.6‰ increase of average *E. excavatum* δ^{18}O (weighted to the number of mono-specific foraminifera per analysis) and decreased A-E index values during the 1950s of BR4 coincide with severely reduced Brazos River discharge (Fig. 23). The

reduction of discharge is the result of a Texas drought that lasted from 1948 to 1957 (Norwine and Bingham, 1985), termed the Little Dust Bowl (Opie, 1989). During the drought, average annual Brazos discharge measured 941 m^3s^{-1}, much lower than usual discharge of ~2400 m^3s^{-1} (USGS River Gauge 08114000).

We can calculate the salinity change associated with a 0.6‰ shift in $\delta^{18}O$ assuming two-component mixing between Brazos River water with a $\delta^{18}O$ of -2.7‰ and salinity of 0 and Gulf of Mexico seawater with a $\delta^{18}O$ of 1.1‰ and salinity of 36. The relation is:

$$\text{Salinity} = 9.7\ \delta^{18}O + 26.3$$

Using this relationship, the 0.6‰ increase of *E. excavatum* $\delta^{18}O$ translates to a salinity increase of nearly 6. On the Texas shelf, the two dominant regional fresh water influences are the Brazos and Mississippi-Atchafalaya Rivers. The general coastal circulation advects Mississippi-Atchafalaya discharge to the Texas shelf from fall to spring, and reverses during summer (Nowlin et al., 2005). In an oxygen isotope study of Texas shelf waters, DiMarco et al. (submitted) found that the source of fresh water was mainly Brazos waters during July of 2007 and predominantly Mississippi-Atchafalaya waters during May of 2008, when BR4 and BR5 were collected.

The influence of freshwater discharge on the $\delta^{18}O$ of foraminiferal tests will depend on the $\delta^{18}O$ of the freshwater source. The Brazos River and Mississippi-Atchafalaya River systems have different $\delta^{18}O$ signatures due to the differences in latitude of their drainage basins (Kendall and Coplen, 2001). Mississippi-Atchafalaya

River waters average -5.8‰ (assuming 70% Mississippi and 30% Atchafalaya flow determined at the Old River Control Structure)(Lee and Veizer, 2003). Brazos River waters exhibit an average of -2.7‰ (B.K. Coffman and E. Grossman, unpubl. data, 2010). Considering that Mississippi-Atchafalaya discharge influences the salinity of Texas' coastal waters, it is likely that the low *E. excavatum* $\delta^{18}O$ of -0.9‰ prior to the LDB is reflects the lower $\delta^{18}O$ of Mississippi-Atchafalaya river water.

In addition to the $\delta^{18}O$ excursion and the low A-E index, the late 1950s interval is marked by an increase in average *E. excavatum* weight of up to 10 µg (Fig. 20). In marginal environments, lowered salinity is generally associated with reduced well-being of the marine macrofauna (Remane and Schlieper, 1971), leading to reduced lifespans and growth, and quick reproductive maturity. Although not applicable to all microfauna, Poag (1978) found that *Elphidium* secrete smaller tests in lower salinity waters of San Antonio Bay due to the shortened time in reaching reproductive maturity. In contrast, *A. parkinsoniana* have been shown to produce large shells when salinity exceeds or falls short of the optimum range (Bradshaw, 1957). Therefore, we contend that increased weights and presumably later onset of sexual maturity in *E. excavatum* reflect higher salinity bottom waters associated with reduced Brazos River discharge. No correlation between *A. parkinsoniana* or *E. excavatum* weight and $\delta^{18}O$ or $\delta^{13}C$ was found, so positive isotopic excursions do not appear to be related to specimen size.

Limited stratification and hypoxia have been associated with reduced Mississippi-Atchafalaya discharge on the Louisiana shelf (Rabalais et al., 2002a), and concordantly, we expect that severely reduced Brazos River discharge to be associated

with limited stratification and hypoxia in Texas shelf waters. The failure of *A. parkinsoniana* $\delta^{18}O$ and $\delta^{13}C$ to record this event is likely related to vertical migration within sediments and warmer growth temperatures. Living *Ammonia* have been observed at up to 25 cm depth in sediments (Moodley, 1990; Moodley and Hess, 1992), thus obscuring any temporal record. Although the fine clay-rich character of shelf sediments would likely impede the vertical migration of Ammonia. The warmer growing period of *A. parkinsoniana* may be reflecting summer conditions of limited wind-driven mixing and stratification (Nowlin et al., 2005) so that *A. parkinsoniana* may be pre-disposed to yielding $\delta^{18}O$ values associated with higher bottom water salinities.

Carbon isotopes

With the exception of three values, all $\delta^{13}C$ values of BR4 *A. parkinsoniana* lie within a range of -2 to -3.5‰ (Fig. 22). Two factors likely contribute to the constant range of values: infaunal habitat of varying depth, and influence of aerobic and anaerobic respiration in hypoxic to anoxic pore waters. While *Ammonia* have not been shown to exhibit significant $\delta^{13}C$ vital effects, they often exhibit low $\delta^{13}C$ due to microhabitat effects (Chandler et al., 1996). H_2S from bacterial sulfate reduction has been detected by odor in nearby sediments (Harper et al., 1981) and also occurs beneath the Mississippi River delta plume of the Louisiana shelf (Lin and Morse, 1991). The preference of *A. parkinsoniana* for low-oxygen pore waters provides an explanation for negative $\delta^{13}C$ values with limited variability. Furthermore, *A. becarri*, a species synonymous with *A. parkinsoniana,* has been observed burrowing up to 25 cm in sediments to inhabit an optimal habitable zone (Moodley and Hess, 1992). Therefore, the

depth profiles for both $\delta^{13}C$ and $\delta^{18}O$ of *A. parkinsoniana* may be significantly obscured, but the correlation between A-E index values of both cores in addition to the character of shelf sediments suggests burrowing effects are limited.

E. excavatum $\delta^{13}C$ values are considerably lower and more variable than those of *A. parkinsoniana*. The preference of *E. excavatum* for more oxygenated waters relative to *A. parkinsoniana* suggests that *E. excavatum* specimens would not burrow to sediment depths strongly influenced by ^{13}C-depleted pore waters. The $\delta^{13}C_{DIC}$ of northern Gulf of Mexico sub-pycnocline waters is largely controlled by aerobic respiration of organic carbon (Chapter II). Therefore, *E. excavatum* $\delta^{13}C$ values may track increased bottom water respiration. However, *E. excavatum* $\delta^{13}C$ has also been shown to exhibit a varying vital effect of up to nearly 4‰ lower than equilibrium calcite (McCorkle et al., 1997). The offset of BR4 and BR5 *E. excavatum* values from $\delta^{13}C_{DIC}$ suggests a similar vital effect applies to Texas shelf *E. excavatum*, therefore obscuring indications of respiration and bottom water DO.

Although a record of respiration is not captured by *E. excavatum*, the influence of the Little Dust Bowl is likely reflected by the positive shift in $\delta^{13}C$ values between 9 and 10 cm of core BR4. In general, river water $\delta^{13}C_{DIC}$ values are much lower than seawater values due to the influence of terrestrial organic carbon and upstream weathering of continental rocks (Drever, 1997), thus the increase of *E. excavatum* $\delta^{13}C$ is likely tracing a shift to more open ocean conditions (where $\delta^{13}C_{DIC} \approx 0.5$‰; J. Strauss, unpubl. data).

Conclusions

Relative abundances of *E. excavatum* and *A. parkinsoniana* (A-E index) reveal low-oxygen conditions proximal to the delta at least since its construction in 1929. Both cores exhibit lowered A-E values that correspond to dramatically reduced Brazos River discharge caused by a severe drought in the Texas mainland from 1948-1957 (the Little Dust Bowl) and reduced discharge of the Brazos River. In addition to low A-E index values, higher oxygen and carbon isotope values of *E. excavatum* indicate a transition to more open ocean salinities concurrent with this event. This event is also marked by an increase in *E. excavatum* test weight and size, suggesting a more hospitable (i.e. oxygenated) environment. Thus, we conclude that a shift to oxygenated, more marine conditions coincided with the near decade long drought.

The preference for oxygenated bottom waters of *E. excavatum* suggests a near surface sediment habitat. The $\delta^{13}C$ of *E. excavatum,* however, exhibit significant vital effects that limit interpretation of bottom water respiration and estimates of DO. The preference for low-oxygen environments exhibited by *A. parkinsoniana* equates to $\delta^{13}C$ values obscured by consistent microhabitat effects from pore waters influenced by increased aerobic and likely anaerobic respiration (i.e. sulfate reduction). While vertical migration is observed in *A. parkinsoniana*, the temporal correlation of A-E index values between sites with disparate sedimentation rates implies that vertical migration at the study localities was limited.

CHAPTER V

CONCLUSIONS

The oxygen and hydrogen isotopic characterization of April, 2008 shelf surface waters reveal mixing with both Mississippi and Atchafalaya discharge, with the former being of greater influence. By July, the $\delta^{18}O$ and δD of waters are too high to be explained by mixing with unmodified Mississippi or Atchafalaya waters. This is interpreted to be a result of enhanced evaporation in the Atchafalaya Basin caused by increased summer irradiance. Assuming this interpretation, the increased $\delta^{18}O$ and δD values provides qualitative evidence that Atchafalaya River water is the dominant freshwater source during July on the continental shelf off Terrebonne and Atchafalaya Bays. Prior shelf $\delta^{18}O$ observations (Wagner and Slowey, 2011) yield very similar results interpreted to be tracing full Atchafalaya River influence. This scenario is supported by the coastal circulation paradigm, where current direction is westward from fall through spring and shifts to an easterly direction during the summer. This results in the buildup of Atchafalaya discharge over the Louisiana shelf and the migration of Mississippi discharge towards the Florida shelf and offshore.

$\delta^{13}C_{DIC}$ of surface waters are also influenced by river discharge, although independent river sources cannot be identified. In bottom waters, $\delta^{13}C_{DIC}$ and DO below the pycnocline correlate due to aerobic respiration of ^{13}C-depleted organic carbon. Mass balance calculations have provided quantitative estimates for the carbon isotope compositions of respired carbon in bottom waters. Bottom waters indicate that

terrestrially derived organic carbon is respired in inshore waters of 10 m depth, and that marine organic carbon is respired at 20 m and greater depths. These calculations correspond to inshore delivery of labile OC by the Atchafalaya. Middle depth waters indicate significant water column respiration near the pycnocline, however the $\delta^{13}C$ of respired carbon could not be calculated, likely owing to reoxygenation from mixing of surface waters. Nevertheless, these data justify the importance of water column respiration as a component of hypoxia formation.

Oxygen and carbon isotopes of mollusks collected from below 10 m on the Texas and Louisiana shelves are not severely influenced by low salinity waters. Their isotopic profiles appear to accurately record seasonal temperatures and track shifts of the $\delta^{13}C_{DIC}$ of DIC associated with water column mixing and benthic respiration.

Stable isotope analyses of nearshore Louisiana shelf *Strombus* shells indicate mixing of the water column at 7 m depth. Isotope profiles of historically collected *C. austini* span between three and four years. *Conus austini* $\delta^{13}C$ records exhibit a subdued respiration signal translating to a minimal decrease in DO, indicating no hypoxia at their localities from 1969-1970. *Conus austini* records also show that the water column mixing caused by hurricane Camille significantly lowered salinity at 24 m depth but had little influence at 30 m, and that the water column restratified roughly 14 days following the storm. Texas shelf *P. colymbus* yield isotopic records only spanning about one year. However, their isotopic profiles may be tracking benthic respiration during the summer of 2009.

Additionally, comparison of *C. austini* and *P. colymbus* $\delta^{13}C$ values with published $\delta^{13}C$ values of *C. erminius* shells from the Stetson bank reveal a decrease in shelf water $\delta^{13}C_{DIC}$ associated with the intrusion of ^{13}C reduced fossil fuel CO_2. The $\delta^{13}C_{DIC}$ depletion rates calculated from shells in this study are nearly double global averages and are 30% higher than previously reported rates from Gulf of Mexico waters.

Relative abundances of *E. excavatum* and *A. parkinsoniana* reveal low-oxygen conditions proximal to the Brazos River delta. Both cores exhibit lowered A-E values that correspond to dramatically reduced Brazos River discharge caused by the Little Dust Bowl, a severe drought in the Texas mainland from 1948-1957. This event is also marked by an increase in *E. excavatum* test weight and size, suggesting a more hospitable (i.e. oxygenated) environment. Moreover, higher oxygen and carbon isotope values of *E. excavatum* indicate a transition to more open ocean salinities concomitant with this event. In total, data suggests that that a shift to oxygenated, more marine conditions coincided with the Little Dust Bowl.

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APPENDIX 1

STABLE ISOTOPE MEASUREMENTS AND SALINITY AND DO OBSERVATIONS OF 2008 LOUISIANA SHELF WATERS

Date	Station	Latitude	Longitude	Depth (m)	Salinity	DO (ml L^{-1})	$\delta^{18}O$ ‰	δD ‰	$\delta^{13}C$ ‰
4/16/2008	12C	29.0608	-91.7689	0	25.41	5.1	-1.0	-6	-
4/16/2008	12C	29.0608	-91.7689	3.5	28.13	4.65	-0.4	-	-
4/16/2008	12C	29.0608	-91.7689	8.5	28.47	4.29	-0.4	-	-
4/16/2008	13C	28.9376	-91.8739	0	27.9	4.8	-0.5	-4	-0.7
4/16/2008	13C	28.9376	-91.8739	10	28.29	4.83	0	-	-0.2
4/16/2008	13C	28.9376	-91.8739	19.5	35.89	3.43	1.2	-	0.2
4/16/2008	1B	28.8451	-90.7841	0	24.41	5.8	-1.3	-9	-
4/16/2008	1B	28.8451	-90.7841	15	34.67	0.42	-	-	-
4/16/2008	1C	29.1773	-92.3330	0	26.92	5.46	-0.8	-4.	0.5
4/16/2008	1C	29.1773	-92.3330	5	26.92	5.49	-0.6	-	-
4/16/2008	1C	29.1773	-92.3330	10	26.90	5.64	-0.6	-	0.6
4/16/2008	2C	29.0610	-92.3757	0	26.45	5.63	-0.8	-6	0.3
4/16/2008	2C	29.0610	-92.3757	10	28.27	5.23	-0.7	-	0
4/16/2008	2C	29.0610	-92.3757	20	34.90	2.8	0.4	-	-0.2
4/16/2008	33D	29.2014	-92.7054	0	30.71	4.58	0.2	0	-0.2
4/16/2008	33D	29.2014	-92.7054	10	30.83	4.69	0.2	-	-0.2
4/16/2008	33D	29.2014	-92.7054	17.5	34.74	3.29	0.9	-	0.1
4/16/2008	35D	29.2985	-92.4626	0	27.68	5.15	-0.5	-3	0.1
4/16/2008	35D	29.2985	-92.4626	5	27.67	5.24	0.9	-	0.4
4/16/2008	35D	29.2985	-92.4626	10	28.21	5.15	-0.4	-	0.6
4/16/2008	36D	29.1722	-92.5515	0	29.50	4.85	-0.2	-3	-0.9
4/16/2008	36D	29.1722	-92.5515	10	29.77	4.88	-0.1	-	0.3
4/16/2008	36D	29.1722	-92.5515	18	34.80	3.29	0.8	-	-0.1
4/16/2008	3B	28.5823	-90.7796	0	29.35	5.75	-0.2	-3	0.7
4/16/2008	3B	28.5823	-90.7796	10	31.41	5.12	0.8	-	0.2
4/16/2008	3B	28.5823	-90.7796	19	35.53	2.82	1.3	-	0.1

4/16/2008	4B	28.8038	-90.6811	0	23.25	5.74	-1.5	-11	-
4/16/2008	4B	28.8038	-90.6811	10	30.98	3.65	-	-	0.1
4/16/2008	4B	28.8038	-90.6811	18	34.92	1.3	1.0	-	-
4/16/2008	4C	29.1390	-92.1133	0	26.94	4.57	-0.7	-4	-1.0
4/16/2008	4C	29.1390	-92.1133	5	26.94	4.67	-0.8	-	-
4/16/2008	4C	29.1390	-92.1133	12	27.00	4.58	-0.6	-	-0.8
4/16/2008	5C	29.0213	-92.1773	0	27.89	5.02	-0.3	-4	0
4/16/2008	5C	29.0213	-92.1773	10	28.07	5.11	-0.5	-	-0.1
4/16/2008	5C	29.0213	-92.1773	19.5	35.61	3.12	1.4	-	0
4/16/2008	6B	29.0213	-90.6823	0	26.51	6.02	-0.4	-6	-
4/16/2008	6B	29.0213	-90.6823	10	34.70	3.62	0.8	-	-
4/16/2008	6B	29.0213	-90.6823	17.5	35.39	3.19	1.1	-	0.1
4/16/2008	7B	28.9625	-90.5474	0	23.15	6.25	-1.5	-11	0
4/16/2008	7B	28.9625	-90.5474	0	21.89	6.26	-1.8	-11	-
4/16/2008	7B	28.9625	90.5474	5	21.89	5.97	-1.7	-	-
4/16/2008	7B	28.9625	90.5474	8	26.23	5.75	-0.6	-	-0.5
4/16/2008	7B	28.9625	90.5474	11	26.41	2.87	-0.7	-	-
4/16/2008	7B	28.9625	90.5474	12	33.78	3.71	0.2	-	-
4/16/2008	7C	29.1228	-91.9104	0	25.39	4.97	-1.1	-6	-
4/16/2008	7C	29.1228	-91.9104	5	25.39	4.97	-0.9	-	-
4/16/2008	7C	29.1228	-91.9104	9.5	25.39	5.14	-	-	0.3
4/16/2008	8B	28.8424	-90.5665	0	22.54	5.69	-0.8	-6	0.1
4/16/2008	8B	28.8424	-90.5665	10	24.68	2.93	-1.7	-	-0.2
4/16/2008	8B	28.8424	-90.5665	17	35.15	2.55	-	-	-0.4
4/16/2008	9B	28.7216	-90.5665	10	33.69	3.75	-	-	-0.1
4/16/2008	9B	28.7216	-90.5665	17	34.32	2.996	0.7	-	-0.3
4/16/2008	BC11	28.6423	-91.1284	0	31.98	5.74	0.4	-1	1.0
4/16/2008	BC11	28.6423	-91.1284	10	32.90	5.4	0.9	-	0.7
4/16/2008	BC11	28.6423	-91.1284	19	35.91	2.92	1.3	-	0.1
4/16/2008	BC12	28.7386	-91.3763	0	29.90	4.63	-	0	-0.4
4/16/2008	BC12	28.7386	-91.3763	10	34.58	3.83	0.9	-	0.2
4/16/2008	BC12	28.7386	-91.3763	19	35.63	3.11	1.1	-	-0.1
4/16/2008	BC13	28.8064	-91.4990	0	27.96	4.74	-1.3	-9	0.1

4/16/2008	BC13	28.8064	-91.4990	10	35.37	3.88	1.1	-	0.3
4/16/2008	BC13	28.8064	-91.4990	20	35.80	3.3	1.4	-	0.3
4/16/2008	BC1A	28.8806	-91.7373	0	25.55	5.24	-1.1	-6	-1.0
4/16/2008	BC1A	28.8806	-91.7373	10	26.02	3.98	-0.5	-	-0.6
4/16/2008	BC1A	28.8806	-91.7373	20	36.1	3.58	1.5	-	0.3
4/16/2008	BC2	28.6774	-91.2607	0	32.16	5.24	-	2	0.8
4/16/2008	BC2	28.6774	-91.2607	10	32.44	5.4	0.5	-	0.5
4/16/2008	BC2	28.6774	-91.2607	18.5	35.78	2.72	1.0	-	0
4/16/2008	BC3	28.6099	-91.0045	0	31.28	6.33	0.7	3	1.2
4/16/2008	BC3	28.6099	-91.0045	10	32.28	5.47	0.4	-	0.4
4/16/2008	BC3	28.6099	-91.0045	19.5	35.93	3.19	-	-	0.1
4/16/2008	BC5	28.8338	-91.2520	0	28.20	5.42	-0.6	-3	-
4/16/2008	BC5	28.8338	-91.2520	5	28.20	5.49	-0.6	-	-
4/16/2008	BC5	28.8338	-91.2520	8.5	28.32	5.5	-0.4	-	-
4/16/2008	BC6	29.0099	-91.4999	0	28.79	4.32	-	-5	-
4/16/2008	BC6	29.0099	-91.4999	5	28.78	4.37	-0.3	-	-
4/16/2008	BC6	29.0099	-91.4999	9	29.05	4.4	-0.25	-	-
7/19/2008	10B	28.6237	-90.5511	0	22.39	2.07	-0.9	-6	-1.2
7/19/2008	10B	28.6237	-90.5511	5	26.42	4.3	-0.1	-	-
7/19/2008	10B	28.6237	-90.5511	15	35.37	2.3	1.1	-	-
7/19/2008	10C	28.8026	-92.1293	10	29.1	4.35	0.1	-	-0.3
7/19/2008	13C	28.9387	-91.8728	0	25.03	4.32	-0.5	-5	-1.2
7/19/2008	13C	28.9387	-91.8728	5	26.37	3.8	0	-	-
7/19/2008	13C	28.9387	-91.8728	15	35.87	2.38	1.1	-	-
7/19/2008	13C	28.9387	-91.8728	20	35.9	2.12	1.2	-	-0.8
7/19/2008	16C	28.8857	-91.7325	0	22.61	4.48	-0.8	-5	-1.4
7/19/2008	16C	28.8857	-91.7325	5	26.23	3.75	-0.5	-	-
7/19/2008	16C	28.8857	-91.7325	10	30.32	2.52	0.8	-	-1.0
7/19/2008	16C	28.8857	-91.7325	15	35.63	2.5	1.1	-	-
7/19/2008	16C	28.8857	-91.7325	20	35.85	2.56	1.1	-	0
7/19/2008	28D	29.3009	-92.9008	10	30.48	3.26	-0.2	-	-0.8
7/19/2008	30D	29.5021	-92.6992	5	28.39	3.91	-0.4	-	-1.9
7/19/2008	36D	29.1716	-92.5507	10	30.39	3.13	0.3	-	-0.7

7/19/2008	38D	28.9001	-92.7492	5	28.79	4.37	0.1	-	-
7/19/2008	38D	28.9001	-92.7492	15	33.02	4.02	0.7	-	-
7/19/2008	3B	28.5816	-90.7780	5	27.93	1.61	-1.0	-	-
7/19/2008	3B	28.5816	-90.7780	10	32.54	3.65	-0.3	-	-
7/19/2008	3B	28.5816	-90.7780	15	35.49	0.85	1.1	-	-
7/19/2008	3B	28.5816	-90.7780	20	36.27	0.73	1.2	-	-0.4
7/19/2008	40D	28.8966	-92.8988	15	33.92	4.23	0.7	-	-
7/19/2008	6B	28.6013	-90.6806	0	15.16	5.96	-2.3	-14	-3.0
7/19/2008	6B	28.6013	-90.6806	10	32.65	2.83	0.7	-	-0.6
7/19/2008	6B	28.6013	-90.6806	15	35.26	0.86	1.0	-	-
7/19/2008	6B	28.6013	-90.6806	20	36.32	0.29	1.1	-	-0.7
7/19/2008	6C	28.9234	-92.2287	20	35.09	0.6	1.0	-	-
7/19/2008	7B	28.9642	-90.5450	10	35.57	0.08	1.0	-	-1.5
7/19/2008	8B	28.8417	-90.5639	0	20.76	4.64	-1.2	-7	-1.5
7/19/2008	8B	28.8417	-90.5639	5	24.9	2.68	0.6	-	-
7/19/2008	8B	28.8417	-90.5639	10	33.4	1.69	0.7	-	-0.4
7/19/2008	8B	28.8417	-90.5639	15	35.67	0.11	1.0	-	-
7/19/2008	8B	28.8417	-90.5639	17	35.64	0.07	1.1	-	-1.6
7/19/2008	9B	28.7214	-90.5516	0	23.7	4.18	-0.7	-	-0.1
7/19/2008	9B	28.7214	-90.5516	5	24.11	3.91	-0.4	-	-4.2
7/19/2008	bc1	28.8806	-91.7373	0	21.09	6.35	-1.0	-6	-1.7
7/19/2008	bc1	28.8806	-91.7373	5	-	5.61	-0.5	-	-
7/19/2008	bc1	28.8806	-91.7373	10	-	2.00	0.7	-	-1.1
7/19/2008	bc1	28.8806	-91.7373	10	-	2.00	0.7	-	-0.9
7/19/2008	bc1	28.8806	-91.7373	15	-	0.60	1.1	-	-
7/19/2008	bc1	28.8806	-91.7373	20	35.92	0.94	1.0	-	-0.7
7/19/2008	bc10	28.6012	-90.8880	0	12.29	8.32	-2.8	-20	-3.8
7/19/2008	bc10	28.6012	-90.8880	5	-	4.01	-0.8	-	-
7/19/2008	bc10	28.6012	-90.8880	10	-	1.39	0.9	-	-0.9
7/19/2008	bc10	28.6012	-90.8880	15	-	1.37	1.12	-	-
7/19/2008	bc10	28.6012	-90.8880	20	35.23	0.98	1.1	-	-0.6
7/19/2008	bc11	28.6423	-91.1284	0	-	10.21	-3.1	-19	-3.8
7/19/2008	bc11	28.6423	-91.1284	5	-	6.15	-0.8	-	-

7/19/2008	bc11	28.6423	-91.1284	10	-	1.42	0.8	-	-1.2
7/19/2008	bc11	28.6423	-91.1284	10	-	1.42	0.8	-	-1.1
7/19/2008	bc11	28.6423	-91.1284	15	35.62	0.27	1.1	-	-
7/19/2008	bc11	28.6423	-91.1284	20	-	0.68	1.1	-	-1.2
7/19/2008	bc12	28.7386	-91.3763	0	19.24	7.07	-1.4	-	-1.9
7/19/2008	bc12	28.7386	-91.3763	5	-	5.58	-0.8	-	-
7/19/2008	bc12	28.7386	-91.3763	10	-	4.31	0.5	-	-0.4
7/19/2008	bc12	28.7386	-91.3763	15	-	2.91	1.1	-	-
7/19/2008	bc12	28.7386	-91.3763	20	-	0.35	1.1	-	-0.9
7/19/2008	bc13	28.8064	-91.4990	0	21.52	6.38	-0.9	-5.	-1.6
7/19/2008	bc13	28.8064	-91.4990	5	-	5.92	-0.5	-	-
7/19/2008	bc13	28.8064	-91.4990	10	-	4.84	0	-	-0.7
7/19/2008	bc13	28.8064	-91.4990	15	-	2.15	1.0	-	-
7/19/2008	bc13	28.8064	-91.4990	20	35.80	2.64	1.2	-	-1.7
7/19/2008	bc2	28.6774	-91.2607	0	16.27	7.50	-1.8	-11	-2.2
7/19/2008	bc2	28.6774	-91.2607	5	-	5.06	-0.4	-	-
7/19/2008	bc2	28.6774	-91.2607	10	-	3.57	0.4	-	-0.8
7/19/2008	bc2	28.6774	-91.2607	15	-	1.66	1.1	-	-
7/19/2008	bc2	28.6774	-91.2607	20	-	0.27	1.1	-	-1.0
7/19/2008	bc3	28.6099	-91.0045	0	-	10.39	-3.5	-23	-5.0
7/19/2008	bc3	28.6099	-91.0045	5	-	3.80	-0.3	-	-
7/19/2008	bc3	28.6099	-91.0045	10	-	0.22	0.9	-	-1.0
7/19/2008	bc3	28.6099	-91.0045	15	-	0.15	1.1	-	-
7/19/2008	bc3	28.6099	-91.0045	20	35.87	0.41	1.1	-	-0.8
7/19/2008	BC6	29.0099	-91.4999	0	-	5.53	-0.6	-5	-2.1
7/19/2008	BC6	29.0099	-91.4999	5	-	4.45	-0.5	-	-1.7
7/19/2008	BC6	29.0099	-91.4999	10	33.19	0.32	0.6	-	-2.1
7/19/2008	BC6	29.0099	-91.4999	10	33.19	0.70	0.6	-	-2.0
7/20/2008	10B	28.6237	-90.5511	10	30.97	0.34	0.5	-	-1.3
7/20/2008	10B	28.6237	-90.5511	20	36.14	1.73	1.1	-	-0.7
7/20/2008	10C	28.8026	-92.1293	0	26.92	4.4	-0.2	-4	-0.8
7/20/2008	10C	28.8026	-92.1293	5	28.51	4.49	-0.1	-	-
7/20/2008	10C	28.8026	-92.1293	15	32.17	3.71	0.4	-	-

7/20/2008	10C	28.8026	-92.1293	20	33.66	0.92	0.8	-	-1.2
7/20/2008	10C	28.8026	-92.1293	25	35.7	1.31	1.2	-	-
7/20/2008	12C	29.0594	-91.7689	0	25.26	4.4	-0.5	-4	-1.4
7/20/2008	12C	29.0594	-91.7689	5	29.57	1.46	0.3	-	-
7/20/2008	12C	29.0594	-91.7689	9	33.57	0.07	0.7	-	-1.9
7/20/2008	13C	28.9387	-91.8728	10	32.21	0.48	0.8	-	-1.3
7/20/2008	16C	28.8857	-91.7325	10	30.32	2.52	0.8	-	-1.0
7/20/2008	1C	29.1760	-92.3306	0	26.16	5.58	-0.3	-3	-0.5
7/20/2008	1C	29.1760	-92.3306	5	26.16	5.69	-0.4	-	-
7/20/2008	1C	29.1760	-92.3306	8	29.02	1.16	-0.2	-	-
7/20/2008	26D	29.5820	-92.8963	0	25.01	5.78	-0.5	-	-1.1
7/20/2008	26D	29.5820	-92.8963	5	25.45	5.02	-0.4	-	-1.8
7/20/2008	26D	29.5820	-92.8963	10	31.62	1.85	0	-	-2.0
7/20/2008	28D	29.3009	-92.9008	0	25.01	4.36	-0.5	-3	-1.3
7/20/2008	28D	29.3009	-92.9008	5	27.27	4.08	-0.2	-	-
7/20/2008	28D	29.3009	-92.9008	15	33.92	0.65	0.3	-	-1.1
7/20/2008	2C	29.0600	-92.3744	0	29.52	4.32	0.2	0	-0.3
7/20/2008	2C	29.0600	-92.3744	5	30.33	4.27	0.3	-	-
7/20/2008	2C	29.0600	-92.3744	10	32.89	4.24	0.8	-	-0.1
7/20/2008	2C	29.0600	-92.3744	16	34.46	3.46	1.0	-	-
7/20/2008	2C	29.0600	-92.3744	20	35.53	0.09	1.1	-	-0.9
7/20/2008	30D	29.5021	-92.6992	0	23.82	4.84	0.1	-	-1.1
7/20/2008	30D	29.5021	-92.6992	10	30.44	1.54	0.2	-	-2.5
7/20/2008	31D	29.3994	-92.5977	0	23.21	4.32	-0.6	-	-1.7
7/20/2008	31D	29.3994	-92.5977	5	24.6	4.65	-0.2	-	-
7/20/2008	31D	29.3994	-92.5977	8	31.98	0.54	0.3	-	-2.0
7/20/2008	33D	29.1993	-92.7023	0	26.23	4.41	-0.2	-	-1.1
7/20/2008	33D	29.1993	-92.7023	5	27.64	4.39	0	-	-
7/20/2008	33D	29.1993	-92.7023	12	31.52	3.92	0.5	-	-0.2
7/20/2008	33D	29.1993	-92.7023	15	33.24	3.96	0.9	-	-
7/20/2008	33D	29.1993	-92.7023	17	34.47	0.99	0.8	-	-0.9
7/20/2008	35D	29.2973	-92.4592	0	23.51	4.25	-0.7	-6	-1.7
7/20/2008	35D	29.2973	-92.4592	5	24.48	4.01	-0.5	-	-

7/20/2008	35D	29.2973	-92.4592	9	31.21	2.09	0.2	-	-1.3
7/20/2008	36D	29.1716	-92.5507	0	23.57	4.18	-0.7	-4	-1.6
7/20/2008	36D	29.1716	-92.5507	5	25.99	3.8	-0.4	-	-
7/20/2008	36D	29.1716	-92.5507	15	34.65	0.54	1.0	-	-
7/20/2008	36D	29.1716	-92.5507	20	34.7	0.38	0.9	-	-1.3
7/20/2008	38D	28.9001	-92.7492	0	28.46	4.33	0	-	-0.6
7/20/2008	38D	28.9001	-92.7492	10	31.85	4.38	0.5	-	0.3
7/20/2008	38D	28.9001	-92.7492	20	34.3	3.82	0.9	-	-
7/20/2008	38D	28.9001	-92.7492	25	35.71	2.74	-	-	0.1
7/20/2008	3B	28.5816	-90.7780	0	11.68	5.36	-2.8	-	-4.2
7/20/2008	40D	28.8966	-92.8988	0	29.76	4.31	-	-	-0.9
7/20/2008	40D	28.8966	-92.8988	5	30.24	4.36	0	-	-
7/20/2008	40D	28.8966	-92.8988	10	32.5	4.25	0	-	-0.9
7/20/2008	40D	28.8966	-92.8988	20	34.48	4.18	1.1	-	-
7/20/2008	40D	28.8966	-92.8988	25	35.81	3.34	1.0	-	-0.9
7/20/2008	4C	29.1387	-92.1093	0	24.59	4.32	-0.7	-5	-1.7
7/20/2008	4C	29.1387	-92.1093	0	24.59	4.32	-0.7	-4	-2.0
7/20/2008	4C	29.1387	-92.1093	5	28.22	3.34	0.3	-	-
7/20/2008	4C	29.1387	-92.1093	10	34.45	0.05	1.0	-	-2.3
7/20/2008	5C	29.0225	-92.1667	0	27.83	4.34	-0.1	-1	-0.7
7/20/2008	5C	29.0225	-92.1667	5	28.67	4.37	0.1	-	-
7/20/2008	5C	29.0225	-92.1667	10	32.28	4.18	0.6	-	0
7/20/2008	5C	29.0225	-92.1667	10	32.28	4.18	0.5	-	-0.1
7/20/2008	5C	29.0225	-92.1667	15	35.35	0.17	1.1	-	-
7/20/2008	5C	29.0225	-92.1667	20	35.65	0.07	1.1	-	-1.0
7/20/2008	6B	28.6013	-90.6806	5	23.5	2.3	-0.1	-	-
7/20/2008	6C	28.9234	-92.2287	0	27.2	4.32	-0.2	-	-0.2
7/20/2008	6C	28.9234	-92.2287	5	28.85	4.34	0.2	-	-
7/20/2008	6C	28.9234	-92.2287	10	32.98	4.08	0.7	-	0.3
7/20/2008	6C	28.9234	-92.2287	15	34.26	4.1	0.8	-	-
7/20/2008	6C	28.9234	-92.2287	25	35.94	1.108	1.2	-	-
7/20/2008	7B	28.9642	-90.5450	0	16.15	6.53	-2.0	-12	0
7/20/2008	7B	28.9642	-90.5450	5	24.36	1.07	-0.1	-	-

7/20/2008	7C	29.1233	-91.9091	0	24.8	4.18	-0.5	-	-1.7
7/20/2008	7C	29.1233	-91.9091	5	28.48	3.89	0.1	-	-
7/20/2008	7C	29.1233	-91.9091	9	33.28	0.25	0.7	-	-1.9
7/20/2008	9B	28.7214	-90.5516	10	32.52	1.27	0.6	-	-
7/20/2008	9B	28.7214	-90.5516	16	35.78	2.26	1.0	-	-1.1
7/20/2008	9C	28.9070	-92.0668	0	26.18	4.36	-0.4	-	-0.5
7/20/2008	9C	28.9070	-92.0668	5	27.52	4.41	-0.2	-	-
7/20/2008	9C	28.9070	-92.0668	10	31.8	4.25	0.4	-	0
7/20/2008	9C	28.9070	-92.0668	15	34.43	0.35	1.0	-	-
7/20/2008	9C	28.9070	-92.0668	20	35.99	1.17	1.1	-	-1.0
7/20/2008	9C	28.9070	-92.0668	24	36	1.09	1.2	-	-

VITA

Josiah Strauss, of Montreal, Quebec, received his Bachelor of Science degree in geology from Florida Atlantic University in 2002. In 2005, he earned a Masters of Science in geology from Florida Atlantic University. Josiah began his doctoral studies with the Department of Geology and Geophysics at Texas A&M University in July 2006 and received his Ph.D. in December 2010. His research interests include using stable isotope geochemistry to study anthropogenic influences on environmentally sensitive regions, particularly in the coastal seas. Josiah will be a postdoctoral researcher in the School of Civil and Environmental Engineering at the University of New South Wales in Sydney Australia. He plans a career in academia.

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